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EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,

COMMITTEE ON PAPERS AND PUBLICATIONS.

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PAPERS ACCEPTED FOR PUBLICATION:

Composition of American Kaolins. By Chas. F. Mabery and Otis T. Klooz.

Composition of Certain Mineral Waters in Northwestern Pennsylvania. By A. E. Robinson and Chas. F. Mabery.

Device for Rapidly Measuring and Discharging a Definite Volume of Liquid. By Edward L. Smith.

Table of Factors. By E. H. Miller.

Some Extensions of the Plaster of Paris Method in Blowpipe Analysis. By W. W. Andrews.

Mercuric Chloro-Thiocyanate. By Charles H. Herty and J. G. Smith.

Issued with September Number, 1896.

Proceedings.

CHANGES OF ADDRESS.

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MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The regular monthly meeting of the Rhode Island Section was held at Providence, May 21, 1896, Mr. Charles S. Bush in the chair.

A paper was presented by Mr. William R. Potter, upon "Fallacies in Urine Analysis due to the Presence of Salicylic Acid and its Compounds."

After a brief introduction of the value of urine examination as an aid to the physician in his diagnosis, the reader described in detail the influence salicylic acid had upon the albumin test and the glucose test as commonly practiced. The chief source of error was pointed out to lie in the sparing solubility of salicylic acid in an aqueous solution, and the ease with which its compounds were decomposed by other acids.

The annual meeting of the Rhode Island Section was held at Pawtucket, R. I., on Thursday afternoon, June 11, 1896.

Members met upon the invitation of the presiding officer, Mr. C. A. Catlin, at the Country Club. After dinner the annual election of officers took place. The following were elected for the ensuing year:

Presiding Officer, Mr. Edward D. Pearce; Secretary and

Treasurer, Mr. Walter M. Saunders; Member of the Executive Committee, Mr. George F. Andrews.

The retiring chairman then presented his annual address, taking for his topic, the subject of chemically-applied mechanics, introducing it by brief historical reference to the progress of chemistry, more particularly to the development of apparatus and improvements along the line of chemical manipulation. It appears that after all the same forms of retort and crucible that did service in the time of Zosimus, are still the stereotyped forms of the chemical supply house.

Great progress in recent years in arts dependent upon chemistry, has, however forced the development of apparatus, and the application of mechanical expedients, until there has grown up what may in all truth be called the science of chemically-applied mechanics, practically unrecognized as yet by the training schools of the profession, though covered in a general way by courses offered in chemical engineering. These courses do not meet the case. The real demand is, that chemical students shall have opportunity in training, to pursue the study of practical mechanics as applied to chemical manipulation, simply a new study added to the old curriculum. Illustrating something of the scope of this chemically-applied mechanics, may be cited, hydraulics, for instance, as applied to the handling of liquids, the speaker showing from his own practical experience how the attendant phenomena of the various filtering methods, may, by a general classification, be brought to useful presentation of the whole subject. Further may be cited pneumatics as applied to the manipulation of air draughts, the charging of liquids with gases, etc., strength and adaptability of materials to the construction of apparatus, their acid or alkaline resisting qualities, with effects of saline solutions upon them; heat in its varied application; light in the practical application of its actinic properties; and the milling of materials. Again illustrating particularly, the speaker showed how the attendant phenomena of the various milling processes may be brought under general statements for better consideration.

Generally the scope of chemically-applied mechanics may be stated as the application of mechanical principles to chemical manipulations. The whole subject should be presented to the chemical student in a general way, setting forth at least the fundamentals along these and related lines, expanding into particular detail in the more important, thus broadly laying the foundation for the development and exercise of the inventive faculty in applying mechanical means to special chemical requirements, whether it be in the factory or the research laboratory.

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THE DETERMINATION OF REDUCING SUGARS IN TERMS OF CUPRIC OXIDE.

BY GEORGE DEFREN.

Received July 9, 1896.

IT is now approximately fifty years since alkaline metallic solutions were first used in determining quantitatively the various reducing sugars. During this period of time many investigators have worked on the subject, and much has been done towards perfecting the method of analysis, so that to-day there are several admirable processes in use for the exact estimation of these carbohydrates.

The quantitative methods of determining reducing sugars may be divided into two main classes: those based upon the volumetric plan, and those which depend on a gravimetric estimation of the precipitated cuprous oxide.

Of the first class many processes have been suggested which have met with more or less success. The volumetric methods are mainly used for factory control work, where the progress of some processes require a rapid and fairly accurate idea of the stage of manufacture. In expert hands the volumetric methods are capable of giving excellent and concordant results, and are, therefore, used in the laboratories of many consulting chemists, and even in scientific institutions.

The main objections to the use of the volumetric methods are that each freshly prepared quantity of Fehling solution requires accurate standardization against the same kind of pure sugar as that which is undergoing analysis. Different dilutions and the

time of boiling affect the results materially. The exact determination of the "end point" also requires considerable practice and skill.

On the other hand, the Fehling liquor used in the gravimetric processes need not be made up as accurately as is required for volumetric work. The gravimetric methods, however, ordinarily require more time. A possible loss of cuprous oxide by filtration, and an incomplete oxidation to the higher oxide are also potent factors, though where the requisite degree of care is exercised these need not cause anxiety. The same statement regarding dilution and time of boiling holds true with as much force in gravimetric as in volumetric work.

The gravimetric methods are generally employed for scientific and accurate analytical work. Here the processes are comparatively few, all depending upon the oxidation of the total sugar present in an excess of the alkaline copper solution.

The tables in use for the determination of reducing sugars are mainly constructed in terms of metallic copper. As the amount of metal precipitated per gram of carbohydrate is not a constant for all dilutions of any sugar, specially constructed tables are generally employed. Several such tables have been prepared, as for instance Allihn's table of reduced copper for dextrose, Wein's table for maltose, and Soxhlet's table for lactose, etc.

Various modifications of the alkaline copper solutions are used for the determination of the different sugars, each requiring special treatment. Therefore a chemist in determining the amount of malt sugar in, say beer, must, if he uses Wein's table for maltose, follow exactly Wein's method for the estimation of that sugar.

Where a variety of work is carried on in a laboratory, it is therefore necessary to have several different Fehling solutions on hand for each special kind of determination. If all the tables for the estimation of the different carbohydrates could have been prepared for use under uniform conditions, the existing state of affairs would be much simplified.

In order to supply this need, I have constructed such tables, using a method which I have employed for some time, in deter-

mining reducing sugars. This method, proposed by O'Sullivan[1] in 1876, is used to some extent in England, but as it seems to be not generally known, I here give the procedure in detail:

To fifteen cc. of the copper sulphate solution, prepared as given below, are added fifteen cc. of the alkaline tartrate solution, in an Erlenmeyer flask having a capacity of from 250–300 cc. The mixture is diluted with fifty cc. of freshly boiled distilled water and placed in a boiling water bath for five minutes. Twenty to twenty-five cc. accurately measured from a calibrated burette of an approximately one-half per cent. solution of the sugar to be analyzed, are then run into the hot Fehling liquor and the whole kept in the boiling water bath for from twelve to fifteen minutes. The flask is then removed from the bath and the precipitated cuprous oxide is filtered as rapidly as possible, either through filter paper or asbestos in a Soxhlet's tube or porcelain Gooch crucible, and washed with boiling distilled water until the wash water no longer reacts alkaline. It is ignited and weighed as cupric oxide as described below. The corresponding amounts of dextrose, maltose or lactose are ascertained by reference to the tables at the end of this article. It should be noted that the above directions must be closely followed. The volume of the Fehling liquor and the added sugar solution should be from 100–105 cc.

The Fehling solution used is made up according to Soxhlet's formula, with a very slight modification. 69.278 grams of pure crystallized copper sulphate, pulverized and dried between filter paper, are dissolved in distilled water. It is advantageous to add one cc. of strong sulphuric acid to this, as recommended by Sutton.[2] The whole is then made up to one liter with distilled water and kept in a separate bottle. The alkaline tartrate solution is made by dissolving 356 grams of crystalline Rochelle salt and 100 grams of sodium hydroxide in distilled water and making up to one liter. This is also kept in a separate bottle.

Two methods of filtration of the precipitated cuprous oxide and further treatment are generally adopted. In the first double "washed" filter paper is used; in the other the precipitate is

[1] *J. Chem. Soc.*, **2**, 130, *1876*.

[2] Sutton: Fourth edition, (1882), 256.

retained by a layer of asbestos. After washing the precipitate on the filter paper as above described, it is dried in the usual manner and ignited in a previously weighed porcelain crucible, taking care to burn the filter paper cautiously, heating for fifteen minutes to a red heat, cooling the crucible over sulphuric acid in a desiccator and weighing as cupric oxide. Additional treatment with nitric acid has been found of no practical advantage, the results by direct ignition being very exact, providing the filter paper is slowly burned. The chief objection to the employment of filter paper to retain the precipitated cuprous oxide, is that some of the finely divided particles are liable to go through, thus causing low results.

As a substitute for paper carefully selected asbestos is often used for filtering purposes. To insure a layer of asbestos which shall be kept at constant weight under the action of hot Fehling liquor, it is advantageous to boil the mineral with nitric acid (1.05–1.10 sp. gr.) for a short time, washing the acid out with hot water, and then boiling with a twenty-five per cent. solution of sodium hydroxide. This is also washed out with hot water. Reboiling with the above reagents as before diminishes the liability of leaving any soluble portions. As thus prepared the filtering material may be kept indefinitely under water in a wide-mouthed bottle ready for use.

The objections of some chemists[1] to the employment of asbestos on the ground that it loses weight on using, does not seem to hold, when it is prepared as above. A sample boiled as stated with acid and alkali three times, lost only two-tenths milligram when two "blanks" of hot dilute Fehling solution, as used in the process above described, were passed through the mineral in a porcelain Gooch crucible.

For use, a layer of asbestos, about one centimeter in thickness, is placed in a porcelain Gooch crucible, to retain the finely divided precipitate, which is filtered by means of suction, in the usual manner. The crucible containing the cuprous oxide is then dropped into a triangular frame, made of platinum wire, suspended within an iron radiator, or shell, heated to redness. This quickly and thoroughly dries the asbestos without cracking

[1] Killing: *Ztschr. angew. Chem.*, 431, *1894*: Praeger: *Ztschr. angew. Chem.*, 520, *1894*.

the crucible. After about five minutes the crucible is transferred by means of a pair of nippers to a red hot platinum crucible and heated for about fifteen minutes. It is then quickly transferred to a desiccator near at hand to prevent cracking, allowed to cool and weighed. As cupric oxide is somewhat hygroscopic, it is advantageous to weigh quickly and to keep the balance case as dry as possible. Prolonged heating in the iron radiator would have changed the cuprous oxide to the cupric state. The advantage of transferring the porcelain crucible to a red-hot platinum crucible, is that the oxidation is quickly completed, as a much higher temperature is available.

If pressed for time, another determination can be made in the same crucible without cleaning it. As a rule, it is, however, advisable to wash out the cupric oxide by means of hot nitric acid (1.05–1.10 sp. gr.) and then with hot water. The crucible is then heated, cooled and weighed as before. It must necessarily be weighed, because this treatment with hot nitric acid dissolves some of the asbestos.

If preferred, a Soxhlet's tube may be used to retain the precipitated cuprous oxide. As a porcelain Gooch crucible possessed obvious advantages over this apparatus, I have used it in all my determinations with success.

The cupric reducing powers of dextrose, maltose aud lactose were determined by the method given above. A table for invert sugar was not constructed because most invert sugar determinations are made by double polarization in a saccharimeter.

DEXTROSE.

The "cupric reducing power" of dextrose was first determined. This is defined as "the amount of cupric oxide which 100 parts reduce."[1] This may be represented by $\frac{100\ W}{D}$, in which W is the weight of cupric oxide obtained by the given weight of any sugar, and D the weight of cupric oxide formed by an equal weight of dextrose.[2] Hence, if the amount of cupric oxide formed by one gram of dextrose be known, the amount of cupric oxide reduced by one gram of any other substance, calculated

[1] *J. Chem. Soc.*, 2, 130, *1876*.
[2] *J. Chem. Soc., Trans.*, 606, *1879*.

upon this number as a percentage, will represent the cupric oxide reducing power of the substance, which we denote by the symbol *K*.

The amount of cupric oxide has been determined by O'Sullivan[1] to be 2.205 grams per gram dextrose. The factor for dextrose in terms of cupric oxide is, therefore, the reciprocal of 2.205 or 0.4535. This value, 0.4535, was assumed to be a constant for all amounts of dextrose when used with Fehling's solution in the manner indicated. As such it was a very convenient quantity, it being only necessary to obtain the weight of cupric oxide formed by the action of a dextrose solution, multiply this by 0.4535, and the amount of dextrose corresponding was obtained. No tables are needed if this assumption be true. Consequently the determination of dextrose was indeed a very simple one.

On an extended investigation of this subject, using various amounts of dextrose on the same volume of Fehling liquor in each determination, I find that the value 2.205, above given as representing the quantity of cupric oxide obtained by the action of one gram of dextrose, is not as was heretofore assumed, a constant for all weights of dextrose taken, the amount varying from 2.27 grams cupric oxide per gram dextrose for small quantities of sugar, to 2.22 grams cupric oxide for the largest amount of dextrose permissible. Allihn,[2] boiling his sugar solutions with the Fehling liquor and reducing the cuprous oxide to copper, obtained analogous varying results.

The purity of the dextrose used was first determined, dextrose anhydride being employed. 10.008 grams of anhydrous dextrose were disssolved in distilled water and the solution boiled to prevent birotation. It was then transferred to a flask, the capacity of which at 15.5° C. was 100.08 cc., thus giving a solution which contained 0.100 gram dextrose anhydride per cc.

The specific gravity of the above solution at 15.5° was determined in the usual manner by means of a picnometer with thermometer attached.

Capacity picnometer (at 15.5°) = 55.2055 cc.
Dextrose solution (at 15.5°) = 57.3083 grams.

[1] *Loc. cit.*
[2] *J. prakt. Chem.*, (2), 22, 63.

On calculating from these values we find the specific gravity of a dextrose solution containing ten grams dextrose in 100 cc. to be 1.03809 at 15.5°.

The specific rotatory power was determined by the usual method, a Schmidt and Haensch saccharimeter being used in polarizing the dextrose solution. The polarizations were carried out in a 200 millimeter tube at 20°. To change from the readings of a saccharimeter to the rotary degrees, it is necessary to multiply the reading observed by 0.344, as shown by Reinbach.[1] I have verified this value with concordant results, a Laurent polariscope being used for comparison. The rotation of the above solution was 30.7 divisions. This gives by means of the usual formula $-[\alpha]_D^{20} = \frac{\alpha v}{lw}$—a specific rotatory power of 52.8°, which is in accordance with that obtained by other observers.[2] The dextrose used was consequently pure.

For the determination with Fehling liquor, twenty-five cc. of the dextrose solution at 15.5° were accurately measured from a calibrated burette and made up to 500 cc. with distilled water at the same temperature. This consequently gave a solution, each cubic centimeter of which contained five milligrams dextrose. Various quantities of this were then taken to ascertain the cupric reducing power of dextrose. The results in detail are given below. In each case the combined volumes of the Fehling liquor and the sugar solution were made up to 105 cc. as described above.

Milligrams dextrose.	Cupric oxide obtained.	Cupric oxide per gram dextrose.	Dextrose equivalent.	Mean dextrose equivalent.
12½	0.0283	2.264	0.4416	0.4401
12½	0.0285	2.280	0.4386	
25	0.0569	2.276	0.4393	0.4419
25	0.0565	2.260	0.4425	
50	0.1129	2.258	0.4429	0.4440
50	0.1123	2.246	0.4452	
62½	0.1407	2.251	0.4443	0.4449
62½	0.1403	2.245	0.4454	
75	0.1683	2.244	0.4457	0.4462
75	0.1679	2.239	0.4467	

[1] *Ber. d. chem. Ges.*, **27**, 2282.

[2] Pribram: *Monat. f. Chem.*, **9**, 399; Landolt: *Ber. d. chem. Ges.*, **21**, 191.

Milligrams dextrose.	Cupric oxide obtained.	Cupric oxide per gram dextrose.	Dextrose equivalent.	Mean dextrose equivalent.
100	0.2233	2.233	0.4478	0.4483
100	0.2227	2.227	0.4489	
125	0.2776	2.221	0.4503	
125	0.2782	2.225	0.4493	
125	0.2770	2.216	0.4512	0.4503
125	0.2774	2.219	0.4506	
125	0.2777	2.222	0.4500	
140	0.3105	2.218	0.4508	0.4511
140	0.3100	2.215	0.4515	

The foregoing values of the amounts of cupric oxide per gram dextrose are given graphically in curve *A*, Plot I, and the dextrose equivalents of this in *A*, Plot II.

From this we get the amount of dextrose corresponding to a given weight of copper oxide by means of the formula:

$$D = (0.4400 + 0.000037\ W)\,W,$$

in which D is the amount of dextrose, and W the weight of cupric oxide.

The dextrose table given in this article is based on this formula, the values of W varying from 30 to 320.

MALTOSE.

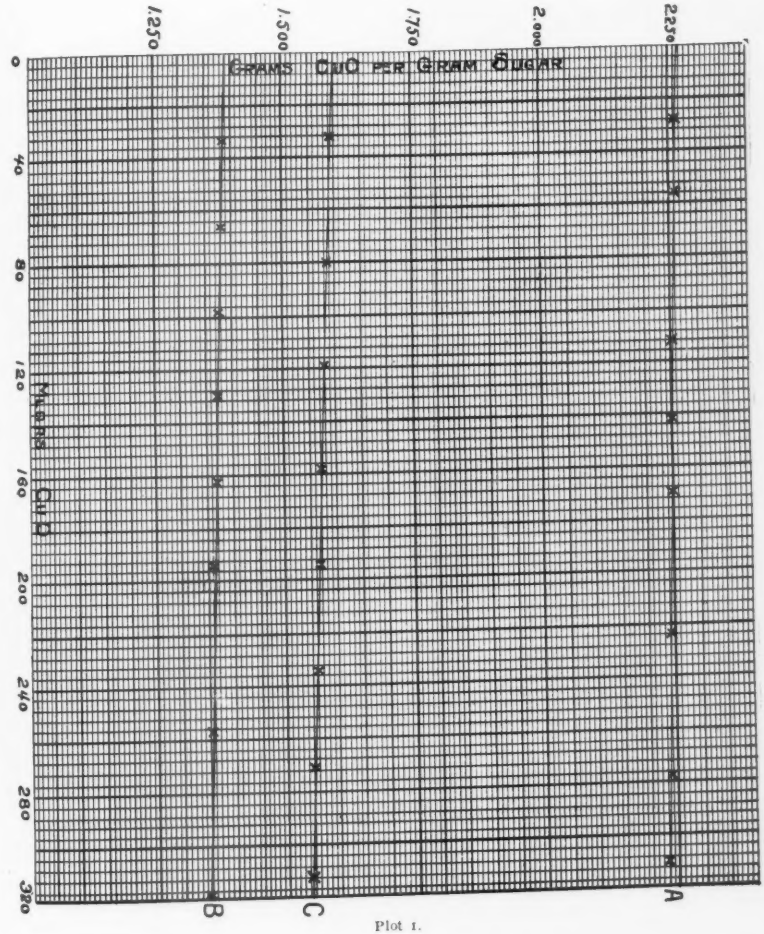
The cupric reducing power of dextrose is given as 100. Using this as a basis, the reducing force of maltose, as given by O'Sullivan,[1] is 65. Brown and Heron[2] place the value somewhat lower, claiming that 61 is more exact. The results which I have obtained agree very well with this latter number.

In the case of maltose, as with dextrose, it was found that the amount of cupric oxide obtained per gram of sugar was not a constant. The cupric reducing power of various amounts of maltose was, however, found to be almost exactly a constant when referred to the cupric oxide from equal weights of dextrose. That is, calling the reducing power of dextrose 100 for different aliquot parts of that sugar, the cupric reducing power of maltose referred to this standard was always 61.

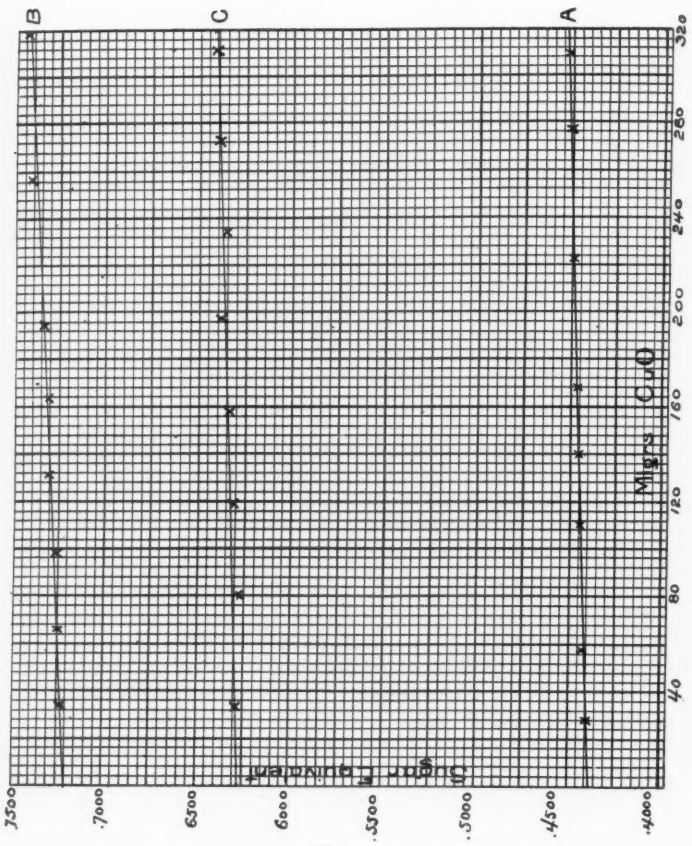
The specific gravity of maltose was determined in the usual manner. 9.7558 grams maltose anhydride were dissolved in distilled water to 100.08 cc. at 15.5°.

[1] *Loc. cit.*

[2] *J. Chem. Soc.*, *1879*, Trans., 619.


1250
1.500
1750
2.000
2250
GRAMS CuO PER GRAM SUGAR
0
40
80
120
160
200
240
280
320
MILLIGRS CuO
B
C
A

Plot 1.


B
C
A
Mgms CuO
Sugar Equivalent
320
280
240
200
160
120
80
40
.7500
.7000
.6500
.6000
.5500
.5000
.4500
.4000

Plot 2.

Maltose solution at 15.5° = 57.3049 grams.

On calculating this we find the specific gravity of the above solution to be 1.03803. For a solution containing ten grams maltose anhydride in 100 cc. it would consequently be 1.03900 at 15.5°.

The specific rotatory power was determined as usual. The rotation of the above solution at 20°, in a 200 millimeter tube, was 74.4 divisions on the saccharimeter scale. This gives $[\alpha]_D^{20} = 136.6°$.

As maltose anhydride is somewhat difficult to prepare, the solutions used to determine the cupric reducing powers were made up to approximately ten per cent. from the maltose hydrate. The specific gravity of the solutions was then determined. Subtracting from this value 1.00000—the specific gravity of water—and dividing the remainder by 0.00390, we get the amount of maltose anhydride in 100 cc. of solution.

Maltose solution at 15.5° = 57.2511 grams,

which gives a specific gravity of 1.03754, or 9.501 grams maltose anhydride in 100 cc.

The solution for Fehling determinations was made in the same manner as the dextrose solutions above. Each cubic centimeter of the diluted maltose solution therefore contained 4.75 milligrams maltose anhydride.

Milligrams maltose.	Cupric oxide obtained.	Cupric oxide per gram maltose.	Maltose equivalent.	Mean maltose equivalent.
23.75	0.0329	1.386	0.7218	0.7240
23.75	0.0327	1.377	0.7263	
47.5	0.0656	1.381	0.7243	0.7253
47.5	0.0654	1.377	0.7263	
71.25	0.0983	1.380	0.7247	0.7263
71.25	0.0979	1.374	0.7278	
95.0	0.1304	1.373	0.7286	0.7297
95.0	0.1300	1.369	0.7308	
118.75	0.1623	1.370	0.7302	0.7319
118.75	0.1619	1.367	0.7336	
142.5	0.1940	1.361	0.7345	0.7354
142.5	0.1934	1.357	0.7369	
190.0	0.2572	1.353	0.7284	0.7395
190.0	0.2566	1.350	0.7406	
237.5	0.3198	1.347	0.7429	0.7433
237.5	0.3193	1.345	0.7437	

The maltose equivalent in terms of copper oxide is shown in *B*, Plot II. From this we get the amount of maltose corresponding to a given weight of cupric oxide by the formula :

$$M = (0.7215 + 0.000061\ W)\,W,$$

in which M is the weight of maltose, and W the amount of cupric oxide obtained. It will be seen that these values make the cupric reducing power of maltose 0.61 that of dextrose.

LACTOSE.

Lactose was investigated in the same manner as the preceding. 10.008 grams lactose anhydride were dissolved in distilled water, boiled, and made up to 100.08 cc. at 15.5°.

The above solution, polarized in a 200 millimeter tube at 20°, gave a rotation of 30.7 divisions. This gives the specific rotary power of lactose of 52.8°.

The amounts of cupric oxide found by the reduction of known weights of lactose were determined as in the previous cases with the following results :

Milligrams lactose.	Cupric oxide obtained.	Cupric oxide per gram lactose.	Lactose equivalents.	Mean lactose equivalents.
20	0.0319	1.595	0.6269	0.6289
20	0.0317	1.585	0.6308	
50	0.0798	1.596	0.6266	0.6274
50	0.0796	1.592	0.6282	
75	0.1188	1.584	0.6313	0.6323
75	0.1184	1.579	0.6334	
100	0.1577	1.577	0.6340	0.6355
100	0.1570	1.570	0.6369	
125	0.1955	1.564	0.6395	0.6379
125	0.1964	1.561	0.6363	
150	0.2345	1.563	0.6397	0.6404
150	0.2340	1.560	0.6410	
175	0.2729	1.560	0.6412	0.6418
175	0.2724	1.557	0.6424	
200	0.3112	1.556	0.6425	0.6430
200	0.3107	1.553	0.6436	

The cupric oxide values per gram lactose are presented graphically in curve *C*, Plot I, while the reciprocals of these quantities are shown in *C*, Plot II. For this latter the amount of lactose corresponding to the weight of cupric oxide obtained is determined by the following :

$$L = (0.6270 + 0.000053\ W)\ W,$$

in which L is the lactose, and W the amount of copper oxide. The acompanying table for lactose is constructed on this basis.

* * * * * * *

It will be seen from the above results that the amount of cupric oxide produced by the action of one gram of reducing carbohydrate on Fehling liquor, in the manner described, is not a constant for all dilutions.

The cupric reducing power of maltose is 0.61 that of dextrose.

The following tables for the determination of the reducing sugars in terms of cupric oxide are based on the analytical results presented above, and can be used in the process outlined in the same manner as any other table for the same purpose:

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
30	13.2	21.7	18.8	57	25.1	41.3	35.9
31	13.7	22.4	19.5	58	25.5	42.1	36.5
32	14.1	23.1	20.1	59	26.0	42.8	37.1
33	14.6	23.9	20.7	60	26.4	43.5	37.8
34	15.0	24.6	21.4	61	26.9	44.3	38.4
35	15.4	25.3	22.0	62	27.3	45.0	39.0
36	15.9	26.1	22.6	63	27.8	45.7	39.7
37	16.3	26.8	23.3	64	28.2	46.5	40.3
38	16.8	27.5	23.9	65	28.7	47.2	40.9
39	17.2	28.3	24.5	66	29.1	47.9	41.6
40	17.6	29.0	25.2	67	29.5	48.6	42.2
41	18.1	29.7	25.8	68	30.0	49.4	42.8
42	18.5	30.5	26.4	69	30.4	50.1	43.5
43	19.0	31.2	27.1	70	30.9	50.8	44.1
44	19.4	31.9	27.7	71	31.3	51.6	44.7
45	19.9	32.7	28.3	72	31.8	52.3	45.4
46	20.3	33.4	29.0	73	32.2	53.0	46.0
47	20.7	34.1	29.6	74	32.6	53.8	46.6
48	21.2	34.8	30.2	75	33.1	54.5	47.3
49	21.6	35.5	30.8	76	33.5	55.2	47.9
50	22.1	36.2	31.5	77	34.0	56.0	48.5
51	22.5	37.0	32.1	78	34.4	56.7	49.2
52	23.0	37.7	32.7	79	34.9	57.4	49.8
53	23.4	38.4	33.3	80	35.4	58.1	50.5
54	23.8	39.2	34.0	81	35.9	58.9	51.1
55	24.2	39.9	34.6	82	36.3	59.6	51.7
56	24.7	40.5	35.2	83	36.8	60.3	52.4

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
84	37.2	61.1	53.0	127	56.5	92.5	80.4
85	37.7	61.8	53.6	128	56.9	93.3	81.1
86	38.1	62.5	54.3	129	57.3	94.0	81.7
87	38.5	63.3	54.9	130	57.8	94.8	82.4
88	39.0	64.0	55.5	131	58.2	95.5	83.0
89	39.4	64.7	56.2	132	58.7	96.2	83.6
90	39.9	65.5	56.8	133	59.1	97.0	84.2
91	40.3	66.2	57.4	134	59.6	97.7	84.9
92	40.8	66.9	58.1	135	60.0	98.4	85.5
93	41.2	67.7	58.7	136	60.5	99.2	86.1
94	41.7	68.4	59.3	137	60.9	99.9	86.8
95	42.1	69.1	60.0	138	61.3	100.7	87.4
96	42.5	69.9	60 6	139	61.8	101.4	88.1
97	43.0	70.6	61.2	140	62.2	102.1	88.7
98	43.4	71.3	61.9	141	62.7	102.8	89.3
99	43.9	72.1	62.5	142	63.1	103.5	90.0
100	44.4	72.8	63.2	143	63.6	104.3	90.6
101	44.8	73.5	63.8	144	64.0	105.0	91.3
102	45.3	74.3	64.4	145	64.5	105.8	91.9
103	45.7	75.0	65.1	146	64.9	106.5	92.6
104	46.2	75.7	65.7	147	65.4	107.2	93.2
105	46.6	76.5	66.3	148	65.8	108.0	93.9
106	47.0	77.2	67.0	149	66.3	108.7	94.5
107	47.5	77.9	67.6	150	66.8	109.5	95.2
108	48.0	78.7	68.2	151	67.3	110.2	95.8
109	48.4	79.4	68.9	152	67.7	111.0	96.5
110	48.9	80.1	69.5	153	68.3	111.7	97.1
111	49.3	80.9	70.1	154	68.7	112.4	97.8
112	49.8	81.6	70.8	155	69.2	113.2	98.4
113	50.2	82.3	71.4	156	69.6	113.9	99.1
114	50.7	83.1	72.0	157	70.0	114.7	99.7
115	51.1	83.8	72.7	158	70.5	115.4	100.4
116	51.6	84.5	73.3	159	70.9	116.1	101.0
117	52.0	85.2	74.0	160	71.3	116.9	101.7
118	52.4	85.9	74.6	161	71.8	117.6	102.3
119	52.9	86.6	75.2	162	72.3	118.4	103.0
120	53.3	87.4	75.9	163	72.7	119.1	103.6
121	53.8	88.1	76.6	164	73.2	119.9	104.3
122	54.2	88.9	77.2	165	73.6	120.6	104.9
123	54.7	89.6	77.9	166	74.1	121.4	105.6
124	55.1	90.3	78.5	167	74.5	122.1	106.2
125	55.6	91.1	79.1	168	74.9	122.9	106.9
126	56.0	91.8	79.8	169	75.4	123.6	107.5

Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.
170	75.8	124.4	108.2	213	95.3	156.3	136.0
171	76.3	125.1	108.8	214	95.8	157.1	136.7
172	76.8	125.8	109.5	215	96.3	157.8	137.3
173	77.3	126.6	110.1	216	96.7	158.6	138.0
174	77.7	127.3	110.8	217	97.2	159.3	138.6
175	78.2	128.1	111.4	218	97.6	160.0	139.3
176	78.6	128.8	112.0	219	98.1	160.8	139.9
177	79.1	129.5	112.6	220	98.6	161.5	140.6
178	79.5	130.3	113.3	221	99.0	162.3	141.2
179	80.0	131.0	113.9	222	99.5	163.0	141.9
180	80.4	131.8	114.6	223	99.9	163.7	142.5
181	80.8	132.5	115.2	224	100.4	164.5	143.2
182	81.3	133.2	115.8	225	100.9	165.3	143.8
183	81.8	134.0	116.5	226	101.3	166.0	144.5
184	82.2	134.7	117.1	227	101.8	166.8	145.1
185	82.7	135.5	117.8	228	102.2	167.5	145.8
186	83.1	136.2	118.4	229	102.7	168.3	146.4
187	83.5	136.9	119.1	230	103.1	169.1	147.0
188	84.0	137.7	119.7	231	103.6	169.8	147.7
189	84.4	138.4	120.4	232	104.0	170.6	148.3
190	84.9	139.1	121.0	233	104.5	171.3	149.0
191	85.4	139.9	121.7	234	105.0	172.1	149.6
192	85.9	140.6	122.3	235	105.4	172.8	150.3
193	86.3	141.4	123.0	236	105.9	173.6	150.9
194	86.8	142.1	123.6	237	106.3	174.3	151.6
195	87.2	142.8	124.3	238	106.8	175.1	152.2
196	87.7	143.6	124.9	239	107.2	175.8	152.9
197	88.1	144.3	125.6	240	107.7	176.6	153.5
198	88.6	145.1	126.2	241	108.1	177.3	154.2
199	89.0	145.8	126.9	242	108.6	178.1	154.8
200	89.5	146.6	127.5	243	109.0	178.8	155.5
201	89.9	147.3	128.2	244	109.5	179.6	156.1
202	90.4	148.1	128.8	245	109.9	180.3	156.8
203	90.8	148.8	129.5	246	110.4	181.1	157.4
204	91.3	149.6	130.1	247	110.9	181.8	158.1
205	91.7	150.3	130.8	248	111.3	182.6	158.7
206	92.2	151.1	131.5	249	111.8	183.3	159.4
207	92.6	151.8	132.1	250	112.3	184.1	160.0
208	93.1	152.5	132.8	251	112.7	184.8	160.7
209	93.5	153.3	133.4	252	113.2	185.5	161.3
210	94.0	154.1	134.1	253	113.7	186.3	162.0
211	94.4	154.8	134.7	254	114.1	187.1	162.6
212	94.9	155.6	135.4	255	114.6	187.8	163.3

Parts. copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose.	Parts. copper oxide.	Parts dextrose.	Parts maltose.	Parts lactose
256	115.0	188.6	163.9	289	130.2	213.6	185.6
257	115.5	189.3	164.6	290	130.6	214.3	186.2
258	116.0	190.1	165.2	291	131.1	215.1	186.9
259	116.4	190.8	165.9	292	131.5	215.9	187.6
260	116.9	191.6	166.5	293	132.0	216.6	188.2
261	117.3	192.4	167.2	294	132.5	217.4	188.9
262	117.8	193.1	167.8	295	133.0	218.2	189.5
263	118.3	193.9	168.5	296	133.4	218.9	190.2
264	118.7	194.6	169.1	297	133.9	219.7	190.8
265	119.2	195.4	169.8	298	134.3	220.4	191.5
266	119.6	196.1	170.4	299	134.8	221.2	192.1
267	120.1	196.9	171.1	300	135.3	221.9	192.8
268	120.6	197.7	171.7	301	135.7	222.7	193.4
269	121.0	198.4	172.4	302	136.2	223.5	194.1
270	121.4	199.2	173.0	303	136.6	224.2	194.7
271	121.9	199.9	173.7	304	137.1	225.0	195.3
272	122.4	200.7	174.4	305	137.6	225.8	196.0
273	122.8	201.5	175.0	306	138.0	226.5	196.6
274	123.3	202.2	175.7	307	138.5	227.3	197.3
275	123.7	203.0	176.3	308	138.9	228.1	197.9
276	124.2	203.7	177.0	309	139.4	228.8	198.6
277	124.6	204.5	177.6	310	139.9	229.6	199.3
278	125.1	205.2	178.3	311	140.3	230.4	199.9
279	125.6	206.0	178.9	312	140.8	231.1	200.6
280	126.1	206.8	179.6	313	141.2	231.9	201.3
281	126.5	207.5	180.2	314	141.7	232.7	202.0
282	127.0	208.3	180.9	315	142.2	233.4	202.6
283	127.4	209.0	181.5	316	142.6	234.2	203.3
284	127.9	209.8	182.2	317	143.1	234.9	203.9
285	128.3	210.5	182.9	318	143.6	235.7	204.6
286	128.8	211.3	183.6	319	144.0	236.5	205.3
287	129.3	212.1	184.2	320	144.5	237.2	205.9
288	129.7	212.8	184.9				

SUPPLEMENTARY TABLE FOR GLUCOSE ANALYSIS.

The amounts of cupric oxide given above are those obtained by the use of absolute weights of sugar. The tables are constructed on this basis. In the case of a mixed product, like commercial glucose, which may be considered made up of the simple bodies, dextrin, maltose, and dextrose, it is far more convenient to determine the total carbohydrates present in solution by means of the specific gravity than by drying the glucose and

obtaining in this way the total solids. For this purpose an arbitrary value is taken which shall represent the influence of one gram of a mixture of the three substances above mentioned on the specific gravity if dissolved to 100 cc. in distilled water. Brown and Heron[1] claim that this influence on the specific gravity of one gram starch conversion product in 100 cc. is 0.00386. This value has been determined to be correct for solutions of cane sugar, and is much used for glucose work.

As above mentioned the specific gravity of a dextrose solution containing ten grams dextrose anhydride in 100 cc. is 1.03809 at 15.5°. To determine the cupric reducing power of a substance using the value 3.86 as a divisor, it therefore becomes necessary to change the figures given in the tables to conform to this new factor, that is, the dextrose equivalents must be multiplied by $\frac{386}{381}$, which has been done for convenience of reference in the following table:

Copper oxide obtained.	Dextrose equivalent.	Copper oxide obtained.	Dextrose equivalent.	Copper oxide obtained.	Dextrose equivalent.
5	0.4461	110	0.4500	215	0.4540
10	0.4463	115	0.4502	220	0.4542
15	0.4465	120	0.4504	225	0.4543
20	0.4467	125	0.4506	230	0.4545
25	0.4468	130	0.4508	235	0.4547
30	0.4470	135	0.4510	240	0.4549
35	0.4472	140	0.4512	245	0.4551
40	0.4474	145	0.4513	250	0.4553
45	0.4476	150	0.4515	255	0.4555
50	0.4478	155	0.4517	260	0.4557
55	0.4480	160	0.4519	265	0.4558
60	0.4482	165	0.4521	270	0.4560
65	0.4484	170	0.4523	275	0.4562
70	0.4485	175	0.4525	280	0.4564
75	0.4487	180	0.4527	285	0.4566
80	0.4489	185	0.4528	290	0.4568
85	0.4491	190	0 4530	295	0.4570
90	0.4493	195	0.4532	300	0.4572
95	0.4495	200	0.4534	305	0.4574
100	0.4497	205	0.4536	310	0.4576
105	0.4498	210	0.4538	315	0.4578
				320	0.4580

[1] *Loc. cit.*

Thus a solution containing 100 milligrams of mixed carbohydrates, using the factor 0.00386, if it formed 200 milligrams cupric oxide by reduction of the Fehling solution in the manner above described, would have a cupric reducing power, or $K_{3.86}$ of 90.68.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

ALUMINUM ANALYSIS.

BY JAMES OTIS HANDY.

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ALTHOUGH the aluminum industry is not a large one in the sense that the iron industry is, it is growing very rapidly. The output of the United States in 1894 was 550,000 pounds, and in 1895 it was about 850,000 pounds. The Pittsburg Reduction Company, with works at New Kensington, near Pittsburg, Pa., and at Niagara Falls, N. Y., is the only American producer of aluminum. The material is made by the electrolysis, in carbon-lined pots, of alumina dissolved in a fused bath of fluorides. The product of each pot is ladled out at intervals and is graded according to the analyses of the Pittsburgh Testing Laboratory, Limited. Some of the aluminum is sold as it is made and some is alloyed to modify its physical properties. Alloys of aluminum with three per cent. nickel, or with three to seven per cent. copper, or similar amounts of zinc are very useful on account of increased strength with only slightly increased specific gravity. The aluminum at present produced with the best ores available contains from

99 to 99.9 per cent. of aluminum.
0.3 to 0.05 per cent. of silicon (combined and graphitic).
0.50 to 0.0 per cent. of copper.
0.20 to 0.0 per cent. of iron.
Carbon is sometimes present in aluminum.

Second grade aluminum contains ninety-six to ninety-eight per cent. aluminum, silicon and iron making up the remainder. Aside from analyses of metallic aluminum, there are required in the pursuit of the aluminum industry, analyses of alloys of copper, nickel, manganese, chromium, tungsten, zinc, and tita-

nium, with aluminum ; aluminum solders, containing tin, zinc, and phosphorus ; aluminum hydrate, bauxite, and electrode carbons ; hydrofluoric acid and fluorides.

ANALYSIS OF COMMERCIAL ALUMINUM. (95 to 99.9 PER CENT. PURE).

In the analysis of aluminum we are offered a choice of solvents.

Solubility of Aluminum : Hydrochloric acid of thirty-three per cent., (*i. e.*, one part of hydrochloric acid of 1.2 sp. gr. to two parts water) is a rapid solvent.

Sulphuric acid of twenty-five per cent. dissolves aluminum completely on long boiling.

Nitric acid of one and two-tenths specific gravity dissolves aluminum on prolonged boiling.

Acid mixture : A mixture of the three acids which we term "Acid Mixture" is made of

100 cc. nitric acid of 1.42 sp. gr.
300 cc. hydrochloric acid of 1.20 sp. gr.
600 cc. sulphuric acid of twenty-five per cent.

It is a very useful solvent for aluminum because it supplies oxidizing conditions during solution and so prevents loss of combined silicon as hydride. The sulphuric acid content of the acid mixture furnishes a means of rapidly dehydrating the silica.

Sodium hydroxide solution of thirty-three per cent. is a useful solvent when it is desired to separate the metallic impurities from the bulk of the aluminum at once. Weaker solutions do not work as quickly or completely. Solution succeeds best in an Erlenmeyer flask.

Fifteen cc. of the sodium hydroxide solution suffice for one gram of aluminum.

Commercial soda lye may be used if dissolved and filtered through asbestos.

OTHER REAGENTS AND STANDARD SOLUTIONS USED IN ALUMINUM ANALYSIS.

Sodium carbonate, chemically pure.

Soda ash : "Solvay" soda ash, a saturated solution in water, filtered.

Powdered zinc: Practically free from iron and copper.

Fifteen per cent. nitric wash: (Fifteen parts 1.42 nitric acid to eighty-five parts water).

Standard potassium permanganate: 5.76 grams in two liters. One cc. equals 0.005 grams iron.

Standard potassium cyanide: Forty-five grams in two liters. One cc. is made to equal 0.005 gram coppper.

SPECIAL APPARATUS.

Two narrow glass tubes, graduated roughly, one to hold one gram of powdered zinc and the other one gram of chemically pure sodium carbonate.

The evaporating dishes which are used are, preferably, about four and a half inches in diameter, and are covered with five-inch glasses.

The Erlenmeyer flasks are of about twelve ounce capacity and furnished with porcelain crucible covers.

THE METHOD.

Determination of Silicon, Iron, and Copper in Commercial Aluminum.—One gram of aluminum drillings is dissolved in a four and a half inch evaporating dish in thirty cc. of "acid mixture." If the drillings are thin it is best to add only fifteen cc. at first. Placing cold water on the cover glass sometimes prevents loss from too energetic foaming. Solution having been completed by warming slightly, evaporate quickly to strong fumes of sulphuric acid and continue heating for five minutes. Experience will show on what parts of the hot plate these solutions can be evaporated without spattering at the time when aluminum sulphate begins to crystallize out. Remove the dishes from the plate by means of an iron fork, and in a few moments add to the contents of each seventy-five to 100 cc. of water and ten cc. of twenty-five per cent. sulphuric acid, break up the residue in each dish with a short, heavy glass rod, and place the dishes back on the hot plate. Boil until all aluminum sulphate dissolves. Add to each dish one gram of metallic zinc powder, measured. Be careful to pour the zinc into the middle of the liquid. If it touches the sides of the dish it sometimes

becomes firmly fixed there. Keep the dish contents at 60° to 70° C. until the zinc has dissolved, leaving the iron reduced and the copper precipitated. Filter and wash well with hot water. Cool, titrate the filtrates with standard potassium permanganate. One cc. equals 0.50 per cent. iron when one gram of aluminum has been used. Placing new receivers under the funnels, treat each residue twice with hot fifteen per cent. nitric acid wash. Wash out with water, and in the solutions thus obtained, titrate the copper with standard potassium cyanide, after adding saturated soda ash solution until the precipitated copper carbonate redissolves. The end point of the titration is very satisfactory. The cyanide solution should be standardized with copper of known purity in about the amount usually found, *viz.*, 0.005 to 0.010 gram. The residue of silicon and silica are burned off in numbered crucibles and each fused with one gram of chemically pure sodium carbonate (measured). The crucible containing the fused mass is placed in fifteen cc. of water in the porcelain dish originally used, and twenty-five cc. of twenty-five per cent. sulphuric acid are added. Solution takes place quickly without separation of silica, and after rinsing out and removing the crucible, the solution is evaporated to five minutes fuming on the hot plate. After cooling add seventy-five to 100 cc. of water and boil to disintegrate the silica. Filter and wash well with water. Burn off and weigh silica and crucible, treat with hydrofluoric acid and a drop of sulphuric acid if impurity is suspected. Evaporate, ignite, and weigh again. Loss equals silica; calculate to silicon.

Determination of Crystalline (Graphitic) Silicon in Aluminum.—Dissolve one gram of aluminum in thirty cc. of thirty-three per cent. hydrochloric acid (two parts of water to one of hydrochloric acid) in a platinum dish; add about two cc. of hydrofluoric acid, stir, and filter at once through a No. 0 nine cm. filter, contained in a funnel which has been thinly coated with paraffin. Wash with water and burn off in a platinum crucible. Fuse with one gram of sodium carbonate, cool in fifteen cc. of water in a four and a half inch evaporating dish. Add twenty cc. of twenty-five per cent. sulphuric acid. Rinse out the crucible. Evaporate to fumes, cool, add seventy-five cc. of water,

boil up and filter off the silica. Wash, ignite, and weigh. Calculate to silicon.

The determinations of silicon, copper, and iron are the every day methods of grading aluminum. It is recognized that sodium and carbon occasionally exist in aluminum, and they are determined by methods described. In certain samples it is desirable to know the approximate percentage of graphitic and combined silicon. These determinations are also described. We determine nitrogen, if present, by a special method.

DETERMINATION OF SODIUM IN ALUMINUM.

One gram of drillings is dissolved in a porcelain evaporating dish in fifty cc. of 1.3 sp. gr. nitric acid and sufficient hydrochloric acid to effect solution. Boil down until all hydrochloric acid has been removed. Rinse the solution into a large platinum dish and evaporate to dryness. Heat over a good Bunsen burner until nitric oxide fumes cease to be evolved. Grind the residue finely. Mix it by grinding with one gram of chemically pure ammonium chloride and eight grams of chemically pure calcium carbonate. Heat the mixture in a large covered platinum crucible. For the first fifteen minutes have a Bunsen burner flame just touching the bottom of the crucible, and for the next forty-five minutes, have the whole crucible heated bright red by a full Bunsen burner flame. Cool, and treat the residue with hot, distilled water until it becomes just friable under pressure. Avoid adding an excess of water beyond that necessary to make the sintered mass just friable. Grind it in a wedgewood mortar and rinse out with hot distilled water. Filter, rejecting the well washed residue, and treat the filtrate at the room temperature with saturated ammonium carbonate solution in slight excess. Stir very thoroughly. The precipitated calcium carbonate is at first flocculent, but on standing for about ten minutes, it becomes crystalline. Filter into a platinum dish ; reject the residue and evaporate the solution on the water-bath to dryness. Heat carefully to dull redness to expel ammonium salts. Dissolve the residue in a little water and add a few drops of ammonium carbonate solution. If this produces a precipitate, add sufficient ammonium carbonate solution to precipitate all of the

remaining lime. Stir well, wait ten minutes, filter, evaporate to dryness, heat to dull redness, and weigh sodium chloride. Deduct any sodium chloride found in a blank determination, using acids, etc., as above, and finally eight grams of calcium carbonate and one gram of ammonium chloride.

$$NaCl \times 0.39316 = Na.$$

Care should be taken when heating up the residue of sodium chloride, etc., after evaporating on the water-bath. If the platinum dish and contents are heated for a few minutes on sheet asbestos on the hot plate before placing over the lamp, spattering may be avoided. Sodium is generally absent from aluminum, but it has been found in amounts as high as 0.20 per cent. and is considered a cause of the occasional deterioration of the metal in water.

DETERMINATION OF CARBON IN ALUMINUM. (MOISSAN'S METHOD MODIFIED.)

Triturate two grams of drillings in a Wedgewood mortar with ten to fifteen grams of mercuric chloride, powdered and dissolved, or partly dissolved, in about fifteen cc. of water. Reaction takes place rapidly and a heavy gray residue is left. Persistent trituration removes the last particles of metallic aluminum. Evaporate on the water-bath to dryness. The dry residue is heated in a current of pure hydrogen to expel mercuric compounds. The remaining material is then placed in a boat in a combustion tube and burned off as in carbon determination in steel. The carbon dioxide is caught as barium carbonate, and the excess of barium hydroxide determined by means of standard acid. We are working on a more generally applicable method for carbon in aluminum.

DETERMINATION OF NITROGEN IN ALUMINUM.

Aluminum, when overheated in re-melting, is believed to have the property of combining with nitrogen. The metal becomes weaker. Moissan's method for determining nitrogen in aluminum may be found in *Compt. Rend.*, **119**, 12. Nitrogen thus absorbed would undoubtedly exist as nitride of aluminum and solution of sodium hydroxide with subsequent distillation

would seem to be the best method of procedure. We are working up this method.

DETERMINATION OF ALUMINUM IN METALLIC ALUMINUM.

Dissolve one gram of metal in thirty cc. of thirty-three per cent. hydrochloric acid in a porcelain dish and evaporated cautiously to complete dryness. Redissolve, by boiling, with ten cc. of concentrated hydrochloric acid and seventy-five cc. of water. Wash into a twelve ounce beaker; dilute to 250 cc. and pass hydrogen sulphide until saturated. Filter into a beaker and boil off hydrogen sulphide. Oxidize by adding one cc. of concentrated nitric acid and continuing to boil for ten minutes. Cool and make the solution up to 500 cc. Remove fifty cc. of the solution, and having diluted to 250 cc. and heated to boiling, add ammonium hydroxide in slight excess and boil well for twenty minutes. Let settle; filter, and wash thoroughly with hot water. It is necessary to wash the precipitate off from the filter, break it up, and wash it back again. Finally burn off in a thin-walled platinum crucible, igniting most intensely, and weighing the instant the crucible and content are cool. We have found that alumina is one of the most difficult oxides to dehydrate completely, and when dehydrated it absorbs atmospheric moisture even more rapidly than calcium oxide does. Moissan prefers to precipitate aluminum by ammonium sulphide. Having prepared a solution in hydrochloric acid, he takes an amount equal to 0.15 gram of aluminum, neutralizes it in the cold with ammonia, and precipitates it by ammonium sulphide, which has been recently prepared. He then digests for one hour, filters, washes with hot water, ignites and weighs.

ANALYSIS OF ALLOYS OF ALUMINUM WITH SMALLER AMOUNTS OF OTHER METALS.

Copper Alloys.—Three to thirty per cent. copper, and no zinc or nickel.

Dissolve one-half gram or one gram in fifteen cc. of thirty-three per cent. sodium hydroxide solution in an Erlenmeyer flask of twelve ounce capacity. If the flask is covered and set in a warm place, solution is complete in a few minutes, even if

the drillings are quite coarse. Dilute to thirty cc. with hot water and filter through a coarse, lintless filter paper (Whitall, Tatum & Co.'s five inch). Wash well with hot water. Dissolve residue, after washing it off the filter paper into a twelve ounce beaker, by warming with five cc. of concentrated nitric acid. Cool, add saturated commercial sodium carbonate solution until re-solution occurs. Titrate with standard potassium cyanide solution to the disappearance of the blue color. Standardize the cyanide for about the same amount of copper.

For commercial reasons, twenty per cent. alloys are made in the reduction pots, and these alloys are subsequently used for making copper alloys of low percentage.

DETERMINATION OF NICKEL IN ALUMINUM ALLOYS.

The three per cent. nickel alloy is now used. The addition of three per cent. of nickel increases the tensile strength of aluminum by several thousand pounds per square inch.

One gram of drillings is dissolved in fifteen cc. of thirty-three per cent. sodium hydroxide solution in a twelve ounce Erlenmeyer flask. Dilute to fifty cc. and filter through a five-inch lintless paper, washing the residue thoroughly with hot water. Rinse the residue back into the flask and add three to five cc. of concentrated nitric acid, and a drop of concentrated hydrochloric acid. Boil, and when dissolved, cool, and make up to 250 cc. In 100 cc. determine the copper by neutralizing with ammonia, adding two cc. of concentrated hydrochloric acid, warming and passing hydrogen sulphide. Filter and wash with ammonium sulphide. Burn it off carefully in a porcelain crucible, and having weighed, dissolve in five cc. of concentrated nitric acid. Then dilute to twenty cc., add excess of sodium carbonate solution and titrate with standard potassium cyanide. Boil the filtrate from the cupric sulphide, oxidize with one cc. of nitric acid, and precipitate with ammonium hydroxide. Do not boil, but digest for a few minutes just below the boiling point. Filter, wash, redissolve in hot fifteen per cent. nitric acid wash. Dilute to 150 cc. and again precipitate with excess of ammonium hydroxide, being careful to avoid boiling or prolonged digestion. Filter and wash. Burn off and weigh ferric oxide, etc. In a second

100 cc. of the main solution, precipitate nickel hydroxide, cupric oxide, ferric hydroxide, etc., by thirty-three per cent. chemically pure sodium hydroxide solution, added in slight excess to the boiling solution. Boil for fifteen minutes, filter, and wash most thoroughly with hot water. Burn off and weigh nickel oxide, cupric oxide and ferric oxide. Deduct cupric oxide and ferric oxide already found. Calculate nickel oxide to metallic nickel.

ANALYSIS OF ALUMINUM-MANGANESE ALLOYS.

Determination of Manganese.—Place one gram of drillings in a twelve ounce beaker. Add thirty cc. of thirty-three per cent. hydrochloric acid (one part of concentrated hydrochloric acid to two of water). When dissolved, add twenty-five cc. of nitric acid (1.42), and boil down to ten cc. Add fifty cc. of colorless nitric acid (1.42) and boil. Precipitate the manganese with powdered potassium chlorate, added cautiously, and proceed as described under manganese in steel by Williams' method.[1]

ANALYSIS OF CHROMIUM-ALUMINUM ALLOY.

Determination of Chromium.—Dissolve one gram in a twelve ounce beaker in thirty cc. of thirty-three per cent. hydrochloric acid, and when dissolved add fifty cc. of sulphuric acid (1.84), and evaporate carefully until fumes of sulphur trioxide escape. Cool, add sixty cc. of water and boil. After five minutes, if all aluminum sulphate has been dissolved, add powdered potassium permanganate until the solution has a distinct pink color. Boil until the excess of potassium permanganate is decomposed. Filter through washed asbestos and determine the chromium in the filtrate as in chrome steel.[2]

ANALYSIS OF TUNGSTEN-ALUMINUM ALLOY.

Determination of Tungsten.—Dissolve one gram in thirty-three per cent. hydrochloric acid in a four and a half inch evaporating dish. Add thirty cc. of nitric acid (1.42) and evaporate to dryness. Redissolve in thirty cc. of hydrochloric acid (1.20), dilute to about ninety cc., and boil for two hours. Filter and wash thoroughly. Burn off and weigh $Si + SiO_2 + WO_3 +$ crucible. Treat with three drops of twenty-five per cent. sul-

[1] Blair's "Chemical Analysis of Iron."

[2] Galbraith's Method. See Blair's "Chemical Analysis of Iron."

phuric acid and about two cc. of hydrochloric acid. Evaporate carefully over an Argand burner, re-ignite, and weigh crucible and silicon and tungstic oxide. Fuse with one gram of sodium carbonate, cool, place in dish, and add fifteen cc. of water and twenty cc. of twenty-five per cent. sulphuric acid, remove crucible and evaporate until white fumes escape. Cool, redissolve in about fifty cc. of water. Filter, wash, ignite, and weigh silica (from silicon), tungstic oxide, and crucible. Treat with sulphuric acid and hydrofluoric acid, evaporate, ignite, and reweigh. Loss equals silica. Calculate to silicon and add to the weight of silica lost by treatment of first insoluble residue. Deduct this sum from the weight of silicon, silica, and tungstic oxide first found and the remainder equals tungstic oxide. Calculate to tungsten.

ANALYSIS OF ALUMINUM-TITANIUM ALLOY.

Determination of Titanium.—Two grams of the alloy in a twelve ounce Erlenmeyer flask are dissolved by addition of fifty cc. of ten per cent. potash solution. Dilute with distilled water to about 125 cc., boil up, and filter as quickly as possible. Wash ten times with boiling water. Burn off the residue in a porcelain crucible, crush it in a Wedgwood mortar, fuse in a large platinum crucible with ten grams of potassium bisulphate. Conduct the fusion exactly as follows: Choose a good Bunsen burner, and protect it from draught by a sheet-iron chimney; make the flame one and a half inches long, and place the triangle carrying the upright crucible just at the point of the flame. Increase the heat gradually until in ten minutes the lower fourth of the crucible is red hot. Allow it to remain at this temperature ten minutes, moving the lid slightly to one side every two minutes, and giving the crucible (held firmly in the tongs) a gentle rotating movement, then turn up the light until the flame reaches the top of the crucible and envelopes it. Five minutes of this treatment melts down any potassium bisulphate, etc., which have risen on the sides. The flame is lowered and the lower fourth heated for ten minutes longer. Cool, dissolve in about 200 cc. of water; filter, rejecting the residue, if ignition and treatment with hydrofluoric acid show it to be only silica.

If it contains anything more, fuse with four grams of potassium bisulphate again. The filtrate contains all the titanic oxide and the ferric oxide. Add ammonia until a slight permanent precipitate is formed, then add dilute sulphuric acid from a pipette or burette until this precipitate just redissolves. Finally add one cc. more of twenty-five per cent. sulphuric acid and dilute to 300 cc. If the solution is high in iron (which will be indicated by its distinct yellow color) sulphur dioxide gas must be run into it until it is decolorized and smells strongly of sulphur dioxide, but if the solution is nearly colorless, indicating a low percentage of iron, only sulphur dioxide water need be added for the reduction. Boil well for one hour, adding water saturated with sulphur dioxide occasionally. Filter off the titanic oxide through double filters and wash well with hot water. Burn off and weigh as titanic oxide. If the precipitate is yellow, indicating the presence of iron, it may be fused with one gram of potassium bisulphate, the fusion dissolved in ten cc. of dilute sulphuric acid, and the iron determined in this solution by reducing with one gram of zinc, and titrating with permanganate. This is not often necessary. Calculate titanic oxide to titanium. $TiO_2 \times 0.6 = Ti$.

DETERMINATION OF ZINC IN ZINC-ALUMINUM ALLOY. FIRST METHOD.

Dissolve one gram in thirty cc. of thirty-three per cent. hydrochloric acid in a twelve ounce beaker. Dilute to 200 cc. and heat nearly to boiling. Pass hydrogen sulphide till all copper is precipitated. Filter and boil off hydrogen sulphide, oxidize with one cc. nitric acid by boiling ten minutes. Add sodium hydroxide solution until neutral, then make barely acid with hydrochloric acid, and stir until the aluminum hydroxide all dissolves. Add ten grams of sodium acetate and 500 cc. of water, boil up, and filter at once. Dissolve the washed precipitate in hydrochloric acid and repeat the acetate separation. Heat the united filtrates to boiling and pass hydrogen sulphide. Filter off the zinc sulphide on double filters, wash thoroughly with hot water. Burn off in a porcelain crucible, and weigh zinc oxide. Calculate to zinc. This method may be used when

only a small quantity of the sample is available, but when this is not the case, it is better to use the method given below.

DETERMINATION OF ZINC IN ZINC-ALUMINUM ALLOYS. SECOND METHOD.

Dissolve one gram of drillings in thirty-three per cent. sodium hydroxide solution in a twelve ounce Erlenmeyer flask. Filter as soon as dissolved through a four inch lintless filter paper. Wash thoroughly with hot water. Rinse the residue of zinc, iron, copper, silicon, etc., back into the flask. This may require 25 cc. of water. Add five cc. of hydrochloric acid and boil. Dilute to 150 cc. with hot water and pass hydrogen sulphide. Filter and boil off hydrogen sulphide, reoxidize by adding one cc. nitric acid and boiling ten minutes. Add sodium hydroxide till neutral, then add dilute hydrochloric acid till just acid, and then ten grams of sodium acetate, and 300 cc. of boiling water, and boil for five minutes. Wash well. If the precipitate is small, resolution and reprecipitation are not necessary. Pass hydrogen sulphide through the filtrate. Filter off zinc sulphide through double filters. Wash well. Ignite in a porcelain crucible, heating finally over the blast, to zinc oxide. $ZnO \times 0.8032 = Zn$.

ANALYSIS OF ALUMINUM SOLDERS.

Determination of Tin, Phosphorus, and Zinc.—Aluminum solders generally contain phosphor-tin, and zinc. As presented for analysis, they usually consist of a soldered joint, from which the solder must be scraped and analyzed. The analysis, therefore, involves a separation of the elements aluminum, zinc, tin, and phosphorus. It is a difficult matter to determine whether aluminum was a constituent of the solder when only a soldered joint is available for examination. It is best to dissolve all adhering aluminum from the pieces chosen for analysis by treatment with thirty-three per cent. sodium hydroxide solution after which the residue is filtered off, dried, and weighed out for analysis. Dissolve or decompose three-tenths to five-tenths gram in a twelve-ounce beaker by means of twenty cc. of nitric acid (1.42). If necessary, five cc. of hydrochloric acid (1.2) may be used to effect complete decomposition. Evaporate to

complete dryness on a hot plate. Cool, add twenty-five cc. of nitric acid (1.13), and boil thoroughly. Filter. The residue contains all of the tin, most of the phosphorus, and possibly some zinc. Burn it off in a porcelain crucible and, after pulverizing the residue in an agate mortar, mix it with two grams of sodium carbonate and two grams of sulphur, fuse it in a covered porcelain crucible over a Bunsen burner for about half an hour. Give it three minutes of gentle blast flame at the last. Cool, boil out with 150 cc. of water in a twelve-ounce covered beaker. Filter and wash. Extract any possible zinc sulphide, etc., from the residue, by dissolving in nitric acid, boiling off hydrogen sulphide, and adding this to the first filtrate obtained after evaporating to dryness with nitric acid. The sodium sulphide solution contains the tin and phosphorus. Add to it hydrochloric acid until just acid. Warm slightly and pass hydrogen sulphide. Filter off stannous sulphide and wash thoroughly with hot water. Burn off in a porcelain crucible and weigh stannic oxide. Calculate to metallic tin. The filtrate from the stannous sulphide is boiled to expel hydrogen sulphide and then oxidized by adding two cc. of nitric acid and boiling for fifteen minutes more. Filter off any sulphur which separates, and in this filtrate, which should amount to only about 100 cc., precipitate the phosphorus by adding pure sodium hydroxide solution till alkaline, then nitric acid till distinctly acid, heating to 85° C., and adding fifty cc. of filtered molybdate solution. Stir or shake well for five minutes, filter on a weighed filter paper, and after washing with one per cent. nitric acid wash, dry at 100° C. and weigh. Yellow precipitate multiplied by 0.0163 equals phosphorus. The nitric acid solution obtained after evaporating the first solution to dryness, etc., is now neutralized with sodium hydroxide solution, and then made just acid with hydrochloric acid. Ten grams of sodium acetate are now added, and 300 cc. of water (hot). Boil up for five minutes, then filter and wash. If the precipitate is of considerable size, it is probable that aluminum was a constituent of the solder. Redissolve it in a little hydrochloric acid, neutralize, acidify, and make a basic acetate separation as before. Precipitate the zinc in the acetate solutions by hydrogen sulphide.

Filter, wash, ignite in a porcelain crucible, and weigh as zinc oxide. Calculate to metallic zinc. Dissolve the precipitate of aluminum acetate in hydrochloric acid, dilute to 250 cc., and precipitate with ammonia. After filtering, washing, igniting, and weighing as alumina, calculate to metallic aluminum. Solders containing lead are sometimes met with. In such cases, evaporate the nitric acid filtrate from the metastannic acid to small bulk, add twenty-five cc. of twenty-five per cent. sulphuric acid, and evaporate until white fumes escape. Cool, add 100 cc. of water, stir, and let stand for an hour in a warm place. Filter and wash with water containing five per cent. of sulphuric acid. Burn off in a porcelain crucible at a low temperature. Reoxidize any reduced lead oxide and restore its sulphur trioxide by adding a few drops of nitric acid and sulphuric acid and evaporating. Finally weigh lead sulphate. Calculate to metallic lead. Zinc is determined in the lead sulphate filtrate.

ANALYSIS OF ALUMINA.

Alumina is made from bauxite or cryolite. It is usually purchased in the hydrated form.

HYDRATED ALUMINA.

Hydrated alumina is analyzed for water, silica and sodium carbonate.

Water.—Ignite one gram in a closely covered crucible, at first gently and then intensely for fifteen minutes over the strongest blast. The loss on ignition includes water and the carbon dioxide of the sodium carbonate. Calculate the carbon dioxide from the sodium oxide found and deduct it from the loss on ignition.

Silica.—Hydrated alumina is soluble in sulphuric acid of 42° B. The silica, however, is left undissolved. 42° B. sulphuric acid is made by mixing 900 cc. of concentrated sulphuric acid with 1290 cc. of water. Five grams of hydrated alumina are treated with twenty-five cc. of 42° B. sulphuric acid and heated until the alumina appears to be all dissolved. Dilute to 100 cc. and boil. Filter, wash, ignite and fuse the residue with one gram of potassium bisulphate and cool. Dissolve in water, filter, wash, ignite, and weigh in cru-

cible, treat with sulphuric acid and hydrofluoric acid, evaporate, ignite and weigh again. Loss equals silica.

Soda.—The method for the determination of soda is the same in calcined and hydrated alumina. The method is that of J. L. Smith, and is described under "Sodium in Aluminum." Calculate sodium chloride to sodium carbonate, if the sample is hydrated, and to sodium oxide if the sample is calcined alumina.

CALCINED ALUMINA.

Water and soda are determined as in hydrated alumina.

Silica.—Fuse one gram of the finely ground alumina with ten grams of potassium bisulphate. If this does not make a clear fusion add two grams of bisulphate and heat up again. Dissolve the fusion when cool in water and filter. Burn off the insoluble residue. Fuse it with one gram of sodium carbonate and cool in fifteen cc. of water in a four and a half inch evaporating dish. Add twenty-five cc. of twenty-five per cent. sulphuric acid. When all soluble matter has dissolved, remove the crucible and evaporate down until sulphuric acid fumes escape. Cool, dilute with water, boil, filter, ignite, and weigh silica plus crucible, treat with sulphuric and hydrofluoric acids, and weigh again. Loss equals silica.

ANALYSIS OF BAUXITE.

Method adopted, May, 1895.

No unusual apparatus or reagents are required.

One and five-tenths grams of very finely ground bauxite (previously dried at 100° C. and bottled), is taken for analysis. Weigh into a five inch porcelain evaporating dish and dissolve in fifty cc. of acid mixture. This mixture is the same as that used for aluminum analysis. Boil the solution down until fumes escape and keep the residue fuming strongly for about fifteen minutes. Cool, add 100 cc. of water, stir and then boil for ten minutes. Filter, wash well with water, receiving the filtrate in a beaker of about 300 cc. capacity. The filtrate and washings should amount to about 175 cc. Burn off the insoluble residue (which consists chiefly of silica, with a little titanic acid, oxide of iron, and alumina) and weigh it in the crucible, add three drops of twenty-five per cent. sulphuric acid and about five cc. of hydro-

fluoric acid and evaporate slowly to dryness. Ignite very strongly and weigh. The loss in weight equals silica. Add to the residue in the crucible one gram of potassium bisulphate and fuse quickly and thoroughly over a Bunsen burner, cool and place the crucible in the beaker containing the main sulphuric acid solution. The small residue from this fusion will be silica, and is to be added to the silica already found. Having obtained the sulphate solution containing all the alumina, ferric oxide and titanic oxide, make it up to 550 cc. and mix. Then fifty cc. will equal three-tenths gram bauxite. Take fifty cc. and dilute to 300 cc. Add two cc. of concentrated hydrochloric acid and ammonia in slight excess, boil for five minutes, let the precipitate settle, filter and wash very thoroughly with hot water. Test the filtrate for further alumina by boiling. Burn off the filter paper and ignite the precipitate very strongly after crushing all the lumps of alumina. Weigh alumina, ferric oxide and titanic oxide.

Titanic Acid.—Take 100 cc. of the original sulphate solution (six-tenths gram), add ammonia until a slight permanent precipitate is formed, then add sulphuric acid from a pipette or burette until this precipitate just redissolves. Finally add one cc. more of twenty-five per cent. sulphuric acid and dilute to 400 cc. If the bauxite is high in iron (which will be indicated by the distinct yellow color of this solution) sulphur dioxide gas must be run into it until it is decolorized and smells strongly of sulphur dioxide, but if the solution is nearly colorless, indicating a low percentage of iron, only sulphur dioxide water need be used for the reduction. Boil well for one hour, adding water saturated with sulphur dioxide occasionally. Filter off the titanic oxide through double filters and wash well with hot water. If the precipitate is yellow, indicating the presence of iron, it can be fused with one gram of potassium bisulphate, the fusion dissolved in water, and the iron determined in this solution by reducing with zinc and titrating with permanganate. This is not often necessary.

Oxide of Iron.—Take fifty cc. of the sulphate solution, add ten cc. of dilute sulphuric acid and one gram of granulated zinc,

and set the beaker in a warm place. When reduced, filter and titrate the iron with standard potassium permanganate. More zinc is used for bauxites high in iron.

METHOD FOR IRON DETERMINATION, USING A LARGER QUANTITY OF BAUXITE. (APPLICABLE TO PUREST ORES).

Place a half gram of the finely powdered ore in a large platinum crucible and add three cc. of twenty-five per cent. sulphuric acid and five cc. of hydrochloric acid, and evaporate very slowly to fumes; drive off the excess of sulphuric acid by heat, boil out the residue with water and add ten cc. of dilute sulphuric acid. Remove the crucible and reduce with zinc, as above, and titrate.

Water and Organic Matter.—Ignite three-tenths gram, cautiously at first and finally very strongly in a covered crucible. The loss of weight equals water and organic matter.

ESTIMATION OF THORIA. CHEMICAL ANALYSIS OF MONAZITE SAND.

BY CHARLES GLASER.

Received July 9, 1896.

SINCE the introduction of the Auer-Welsbach light, the commercial importance of monazite sand has grown greatly, and chemists are now asked to determine the percentage of true monazite, and especially that of thoria, in samples of the sand. This has heretofore been accomplished indirectly; the quantities of iron, titanium and silica were determined and the remainder of the material calculated as monazite. A sample treated in this manner gave the following results:

	Per cent.
Iron oxide	3.50
Titanic acid	4.67
Silica	6.40
Monazite, by difference	85.43
	100.00

The sample contained 18.38 per cent. phosphoric acid, which calculated as cerium phosphate (factor 3.32) equals 61.10 per cent.

From analyses printed in Dana's Mineralogy, it was inferred

that after elimination of rutile and silica, the remainder would be found to consist chiefly of phosphates of the cerium group, but this is not true.

For the determination of the actual composition of the monazite sand in question, it was decided to attempt an estimation of each of its components, by means of methods to be found in the available literature. As chief sources of information, Graham-Otto's Chemistry and Crookes' Select Methods in Chemical Analysis were used; due regard was also given to the work which has appeared in the chemical journals of recent years. I was not able, however, to make an exhaustive examination of the literature.

It became evident that no reliable method could be worked out until examination had been made of all the work which had been done in the field, and it seemed necessary to investigate the whole question. In the following statements of preliminary experiments a large portion of analytical data has been omitted, because otherwise this paper would have been bulky. Only the outlines of a general plan of procedure will therefore be given.

So far as possible, it was my intention to examine all the methods proposed for estimation of thoria, but in one notable instance this could not be done. In Volume XVI of the *American Chemical Journal*, L. M. Dennis and F. L. Kortright describe a method for estimation of thoria by means of potassium hydronitride, KN_3. An attempt to work by the method proved a failure in my hands, partly because of a mishap while preparing the reagent, only enough of which was saved for a single qualitative reaction; but chiefly because Mr. Dennis declined, when requested, to give me further information. He replied that he was not then at liberty to detail his experience, "as the potassium hydronitride process is more than an analytical one. It is a commercial process for the preparation of pure thoria, which is, I think, unequalled by any of the methods employed by the Welsbach chemists, Shapleigh included. Some of them have tried to use the method and have failed. I think I know why they failed. But I do not think it quite fair for them to ask me to help them out of their difficulties."

Although the publication was made in a scientific journal, it

seems to have been but a partial statement. For which reason criticism is invited and the value of the work is thrown somewhat in doubt. No further attempt was made to follow it out.

By means of fusion with alkali carbonates, an attempt was made to separate monazite sand into two parts. According to Wöhler all titanic acid ought to become soluble provided the fusion is made at a sufficiently high temperature. Therefore a blowpipe was used. In later work I employed the highest temperatures afforded by a muffle, and for as many as two hours. But at no time was more than a fraction of the titanic acid rendered soluble in water. Moreover, Wöhler's directions to pour the fusion upon an iron plate, and afterwards to powder it, are not practicable because of loss likely to ensue. It was found best to let the fusion soak in water over night, sometimes even for several days, or until perfect disintegration resulted. But such a procedure may have decreased the solubility of titanic acid in water. Phosphoric acid and alumina (and also silica to a large extent) were completely dissolved out of the fused mass. The portion insoluble in water was rendered soluble by the well known treatment with strong sulphuric acid, and also by fusion with acid potassium sulphate. The solution thus obtained, after being freed from silica, was boiled to separate titanic acid, from four to seven hours during the first experiment. Later, after addition of sodium sulphite, this was accompanied by saturating with hydrogen sulphide, first in the hot and then in the cooled solution. This method is preferable to the first.

After separation of titanic acid and the metals of the fifth group, various methods were tried for separation of thoria from the other earths. It was found that the solution must not be strongly acid when treated with ammonium oxalate for precipitation of thoria and the metals of the cerium group, or traces of thoria will remain in solution. It is best to nearly neutralize with ammonia, and to precipitate in boiling solution.

During the earlier experiments some difficulty was found in keeping in solution all of the zirconia, which is accomplished only by a large excess of the reagent, while yttria and glucina readily form soluble double salts. Under these conditions oxalates of the cerium metals precipitate immediately, while thorium

oxalate separates upon cooling. Attempts to separate thorium oxalate from oxalates of the metals of the cerium group by filtration of the hot solution, gave unsatisfactory results. The oxalates will pass through the filter for a long time. Bumping of the liquid made it impracticable to keep it boiling until the entire precipitate became crystalline. But if large quantities of thoria are to be separated from small ones of the other oxalates the method works well.

After the insoluble oxalates were separated by filtration and were washed with water, they were converted into oxides by heating and were redissolved as sulphates. In this strongly concentrated solution, made nearly neutral by ammonia, an attempt was made to separate thoria from the other metals by boiling with sodium hyposulphite. In no instance was a complete separation effected, but such portions as were obtained proved to be quite pure. The single exception was that in which the whole of the cerium was precipitated, for reasons not ascertained. Attempts were made to free thoria from most of the cerium by fractional precipitation with weak ammonia, but no considerable advantage was gained thereby, since repeatedly the second fraction showed traces of thorium.

To determine the solubility or insolubility of the different substances left in the insoluble residue from fusions, such residue was treated with dilute hydrochloric acid both cold and hot. The solution was found to contain all the iron and titanium, the larger part of the silica, and about one-half of the earths present; these consisted of relatively large portions of zirconia and glucina. Thoria seems not to enter into solution, but is left with the remainder of the earths.

An attempt was made to separate thorium oxalate from the mixed precipitated oxalates, by boiling with ammonium oxalate. Such boiling, filtering and crystallizing yielded oxalates, which after ignition, corresponded to 2.29 per cent. of oxides. The earths were, however, of a deep orange color, and contained both cerium and zirconia. The latter was present because an insufficient quantity of ammonium oxalate had been used in the first precipitation. In the oxalates of the cerium metals found insoluble in the above treatment, the presence of thoria could be

distinctly proven by means of sodium hyposulphite, for which reason the work proved unsatisfactory.

To facilitate a comparison of the more important reactions of the elements herein studied, the table on the next page has been prepared partly from their known behavior, and partly from the results obtained during this investigation.

With the view of obtaining further knowledge of the behavior of thoria, fragments of Welsbach mantles were subjected to analysis. They weighed 0.6591 gram, which, after ignition, fell to 0.6552 gram. Prolonged treatment with boiling sulphuric acid left a residue of 0.0883 gram, which became soluble in water after fusion with acid potassium sulphate. The solutions thus obtained were examined by the same method, but separately, as follows: After neutralizing with ammonia the greater part of the free acid, the solutions were heated to boiling and hot solution of ammonium oxalate was added.

In solution I a precipitate appeared, but dissolved rapidly upon addition of more of the reagent.

In solution II a slight turbidity appeared, there was no precipitate, and it soon became perfectly clear.

Upon cooling, solution I yielded a moderate quantity of a crystalline deposit, while solution II gave a copious one. Both precipitates were collected on one filter, washed, ignited, and weighed. They yielded 0.1124 grams of thoria.

The filtrate from I gave a copious precipitate with ammonia, while that from II gave only a slight one: both of these were washed on one filter, redissolved in dilute hydrochloric acid, and again precipitated by ammonia. An excess of ammonium carbonate entirely dissolved the precipitate. Potassium hydroxide gave a precipitate not soluble in excess of the precipitant, indicating zirconia, the weight of which was 0.5580 gram. An attempt to purify it from occluded alkali, by again precipitating with ammonia, failed through an accident, in which part of the material was lost. Calculating by difference, the weight of zirconia ought to have been 0.5428 gram. Both precipitates were pure white.

Therefore, this analysis afforded the following composition of the mantles: thoria 17.15 per cent., zirconia 82.85 per cent.

TABLE OF REACTIONS OF THE RARER EARTHS.

	KOH or NaOH	K_2CO_3 or Na_2CO_3.	K_2SO_4 or Na_2SO_4.	$Na_2S_2O_3$.	NH_4OH.	$(NH_4)_2CO_3$.	NH_4Cl.	$(NH_4)_2C_2O_4$.	$NH_4C_2H_3O_2$.
Al_2O_3	Ppt., sol. in excess.	Ppt.	Alums.	Ppt. in boiling almost neutral solution.	Ppt.	Ppt.	Ppt. from solution in NaOH.	No ppt.	Nearly neutral solution boiled gives ppt. of basic salt.
BeO_2	Ppt. sol. in excess. Reppt. when boiled or diluted.	Ppt. with difficulty sol. in large excess and in CO_2.	No ppt., no double salt formed. Sol. with difficulty.	No. ppt.	Ppt. insol. in excess.	Ppt. easily sol. in excess. Ppt. on boiling. Uncertain separation from Al_2O_3.	Hydroxide diss. on prolonged boiling NH_3 escapes.	No ppt., double salt easily sol.	?
ZrO_2	Ppt. insol. in excess.	Ppt. slightly soluble in excess. Ppt. by NH_4OH.	Double salt sol. in hot solution. Ppt. of basic salt on cooling, insol. in HCl.	Ppt. hydroxide mixed with S.	Ppt. insol. in excess.	Ppt. sol. in large excess. Reppt'd. on boiling.	No ppt.	Ppt. sol. in excess.	?
Gadolinite earths.	Ppt. insol. in excess.	Ppt. sol. in excess. After some hours insol. double salt separates (Yt).	Conc. solution ppt. sol. in H_2O or K_2SO_4 (not Yt.) Sept. from thoria and cerites.	?	Ppt. insol. in excess.	Ppt. easily sol. in excess. Ppt. insol. double salt after some hours (Yt).	?	Ppt. red granular powder (Er.) from boiling acid solution.	?
ThO_2	Ppt. insol. in excess.	Ppt. sol. in excess. Turbid on heating, clears on cooling.	Double salt insol. in saturated solution K_2SO_4. Sodium salt much more sol.	Only partial ppt., even on long boiling conc. solution.	Ppt. insol. in excess. ThO_2 ppts. before cerites. Crookes.	Like NH_4OH.	No ppt.	Ppt. nearly insol. in acids. Sol. in excess, hot; ppt. on cooling. HCl ppts.	No ppt. prevents completely ppt'n. by $(NH_4)_2C_2O_4$ Partial ppt. by HCl, complete by excess NH_4OH.
CeO	Ppt. insol. in excess.	Ppt. slightly sol. in excess.	Double salt insol. in K_2SO_4 solution.	No. ppt. (?)	Ppt. insol. in excess.	Like NH_4OH.	No ppt.	Ppt. even in rather acid solution. Slightly sol. in large excess of acid.	Oxalate insol.
Ce_2O_3	Excess gives flesh colored ppt.	Ppt. nearly insol. in excess.		No. ppt.	Like KOH.	Ppt. sol. in large excess. Reppt'd. on boiling.	No ppt.	Like CeO.	Oxalate insol.
La_2O_3	Ppt. insol. in excess.	Ppt. nearly insol. in excess.	Double salt sol. with difficulty.	No. ppt.	Ppt.	White ppt. quite insol. in excess.	No ppt.	Ppt. in neutral or ammoniacal (?) solution.	Oxalate insol.
Di_2O_3	Ppt. insol. in excess.	Ppt. nearly insol. in excess.	Double salt sol. with difficulty.	No. ppt.	Ppt.	Rose colored ppt. quite insol.	No ppt.	Ppt. nearly insol. in oxalic or mineral acids.	Oxalate insol.

The separation of the two earths was effected without difficulty and the thoria was used in the following experiments:

0.0487 gram was weighed, dissolved, and mixed with the solution of cerium metals from a previous experiment. The solution was nearly neutralized with ammonia, heated to boiling, a hot solution of ammonium oxalate added, and the mixture allowed to cool. The precipitate was caught on a filter and washed with cold water, extracted in boiling ammonium oxalate solution, caught on a filter, and washed hot: the filtrate was allowed to cool (precipitate 1). The residue was macerated in a hot solution of ammonium acetate, filtered (residue A), and filtrate examined for thoria, as follows: hydrochloric acid was added to separate thoria as oxalate, which fell in part only and the remainder was obtained by sodium hydroxide (precipitate 2). Both these precipitates afforded but a part of the thoria originally weighed, the greater part being held yet with the cerium metals. The method had failed.

The residue (A) upon the filter was reduced to oxide and dissolved as sulphate. After neutralizing with ammonia, the liquid was heated to boiling, and there was added an excess of ammonium oxalate with some ammonium acetate: after filtering, the filtrate was treated with sodium hydroxide (precipitate 3).

The precipitates, thus obtained in three fractions, were ignited and found to weigh 0.0774 gram, showing that the thoria was very impure. The grayish mass was fused with acid potassium sulphate, and unfortunately, a small fraction of the fused mass was lost. However, from the saved portion a pure thoria, weighing 0.0402 gram. was obtained.

In the next experiment, 0.0343 gram of thoria and 0.1004 gram of impure cerium oxide were dissolved as sulphates, and treated with ammonium oxalate and acetate, as for precipitate 3, next above. By precipitating the filtrate with ammonia there was obtained 0.0360 of impure thoria, which, after purification, weighed 0.0344 gram. Cerium oxide recovered weighed 0.0935 gram.

I desire to call attention to what has been observed frequently during these experiments. If thorium oxalate, held in solution

by ammonium acetate, be precipitated by ammonia, the earth so obtained, when washed with the greatest care and redissolved in a mineral acid, cannot from an almost neutral solution be again completely precipitated by ammonium oxalate; even if the earth had been ignited after re-solution. It will also be found that a considerable increase has occurred in its solubility in liquids containing much potassium or ammonium sulphate. When enough thoria has been collected, it is my intention to further examine this peculiar behavior.

SYSTEMATIC METHOD OF ANALYSIS.

From the analytical data given, the following method has been deduced:

It is essential that the mineral be divided to the greatest possible degree. Prolonged powdering in an agate mortar is indispensable. Solution is effected either by prolonged heating with strong sulphuric acid, or by fusion with acid potassium sulphate. In the latter case, the cooled mass is warmed with so much sulphuric acid that the product, after cooling, may be poured from the crucible. The first method takes more time than the second, but it introduces less of the objectionable potassium salts. It is advisable to fuse only those portions which are insoluble in sulphuric acid.

For estimation of silica the sulphuric acid treatment is preferable, in which case it is best to evaporate once on a sand-bath to dryness to render silica insoluble, and then to add fresh sulphuric acid. The resulting mixture should be added slowly to ice cold water, which dissolves the mass excepting silica and tantalic acid, with possibly traces of titanic acid, thoria, and zirconia. After filtering, the residue should be ignited and weighed. Silica is eliminated by repeated treatment with hydrofluoric acid. Any residue remaining should be moistened with sulphuric acid, to convert the fluorides of the earths into sulphates, which, after ignition at a high temperature, are weighed as oxides, and silica determined by the loss in weight. The residue of tantalic acid, with possibly traces of the bodies mentioned above, is treated with sulphuric acid and hydrofluoric acid. Tantalic acid remains insoluble, and may be filtered off

and weighed. The matter soluble may be added to the main solution.

The original solution is saturated with hydrogen sulphide, first at boiling and then at the ordinary temperature. Titanic acid is precipitated, together with metals of the fifth group. That sodium sulphite assists in the precipitation of titanic acid has not been verified in my work.

When completely settled, the liquid is filtered and the filtrate boiled to expel hydrogen sulphide. Any free acid may be nearly neutralized with ammonia ; to the boiling liquid is added an excess of a boiling solution of ammonium oxalate, as much as 100 cc. of the cold saturated solution for two grams of monazite sand. The excess necessarily must be large. The mixture is then permitted to cool, best for an entire night. The solution will contain phosphoric acid, the oxides of iron, manganese, aluminum, glucinum, yttrium, zirconium, and calcium. In the precipitate will be found thoria and the oxides of the cerium group.

If the bodies in solution are to be estimated, add ammonia to precipitate the metals as phosphates. Filter and wash thoroughly, preserve the filtrate for estimation of phosphoric acid and alumina. Ignite the precipitate and fuse it with mixed carbonates of potassium and sodium. The fused mass is exhausted with hot water, filtered, and the residue well washed with hot water. The filtrate is added to that containing phosphoric acid and alumina.

The remaining oxides and carbonates are dissolved in sulphuric acid and precipitated with ammonia. Lime is estimated in the filtrate therefrom.

When an attempt is now made to dissolve the precipitated hydroxides on the filter by dilute hydrochloric acid, it sometimes occurs that zirconia in part remains. Therefore it is best, after this operation, to incinerate the filter. Then neutralize the solution with ammonia as far as practicable. Pour this slowly, with constant stirring, into a mixture of ammonium carbonate and ammonium sulphide, prepared as follows : To a solution of ammonium carbonate more than enough to neutralize the free hydrochloric acid above indicated, and to hold in solution the

earths to be dealt with, add enough of ammonium sulphide (usually a few cc.) to precipitate the metals of the fourth group. The latter will be precipitated, while zirconia, yttria, and glucinum remain in solution. Iron and manganese may be determined by the usual methods.

If the carbonate solution be boiled for one hour the earths are completely precipitated. They may be caught on a filter and dissolved in hydrochloric acid; or the carbonate solution may be treated directly with that acid, carbon dioxide expelled by boiling, the solution cooled and treated with an excess of sodium hydroxide. Zirconium and yttria are completely precipitated while glucina remains dissolved: to precipitate this, boil the solution one hour.

To separate zirconia from yttria, dissolve the hydroxides in hydrochloric acid, warm, then saturate the solution with sodium sulphate. When cold, zirconia separates in the well-known manner. From the filtrate ammonia separates yttria.

As the earths are apt to occlude alkali salts, it is best to dissolve and again precipitate them (with ammonia) before they are ignited and weighed.

Separation of the precipitated oxalates of thoria and of the cerium group is accomplished as follows: The oxalates are reduced to oxides by ignition, then converted into sulphates, the greater part of the free acid neutralized with ammonia, the solution boiled, and boiling ammonium oxalate added in excess. After a short time (as soon as oxalates of the cerium metals have formed but before the liquid has cooled), a few cc. of solution of ammonium acetate are added. When cold, the entire cerium group is precipitated as oxalates, while thoria remains in solution. After prolonged standing, best over night, the insoluble oxalates are removed by filtration; in the filtrate, precipitate thoria with ammonia in excess, filter, ignite, and weigh.

Separation of cerium from lanthanum and didymium is easily accomplished by the well known method. Pass a current of chlorine through the liquid containing the hydroxides, which have been freshly precipitated by a fixed alkali.

Separation of lanthanum from didymium was not attempted.

An analysis of the monazite sand used in my work, made as indicated in the foregoing notes, gave results as follows:

Titanic acid	4.67
Silica	6.40
Phosphorus pentoxide	18.38
Lead	trace
Alumina	1.62
Lime	1.20
Cerium oxide (CeO)	32.93
Lanthanum and didymium oxides	7.93
Thoria	1.43
Ferric oxide	7.83
Zirconia and yttria	13.98
Glucina	1.25
Tantalic acid	0.66
Not determined	1.72
	100.00

Titanic acid and silica was determined in a separate portion. The determination of tantalic acid was only approximate, since a part of it is dissolved by fusion with acid potassium sulphate, and thus escapes weighing. As several such fusions were made, it is probable that the greater part of the matter "not determined" ought to be reckoned as tantalic acid. The quantity stated was an average of three determinations (minus or plus 0.05) from the residue of repeated fusions.

Through the courtesy of Mr. H. B. C. Nitze, of the Geological Survey of North Carolina, I have received a number of samples of monazite sand mined at various localities in that state. Two of these had been prepared by a new process and were found to be practically free from rutile and garnets. They were excellent material for my methods of analysis, and they gave results as follows:

ANALYSIS OF A COARSE MONAZITE SAND FROM SHELBY, NORTH CAROLINA.

Silica	3.20
Titanic acid	0.61
Cerium metals as CeO	63.80
Phosphorus pentoxide	28.16
Thoria	2.32
Zirconia, glucina, yttria	1.52
Manganese	trace
No iron, alumina, or lime	0.00
	99.61

The color of this sand was honey-yellow.

ANALYSIS OF A FINE MONAZITE SAND FROM BELLEWOOD, NORTH CAROLINA.

Silica	1.45
Titanic acid	1.40
Cerium metals as CeO	59.09
Phosphorus pentoxide	26.05
Thoria	1.19
Zirconia, glucina, yttria	2.68
Tantalic acid	6.39
Iron and manganese oxides	0.65
Alumina	0.15
	99.05

The color of this sand was honey-yellow.

LABORATORY OF LEHMANN & GLASER,
BALTIMORE.

[CONTRIBUTIONS FROM METALLURGICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO.]

THE EFFECT OF AN EXCESS OF REAGENT IN THE PRECIPITATION OF BARIUM SULPHATE.

BY C. W. FOULK.

Received July 6, 1896.

"EXCESS of reagent" is a term often used by writers in quantitative chemistry, and the necessity in any given case for adding more of a precipitating reagent than is just sufficient for complete reaction is well known to analysts; but what constitutes such excess, whether it differs for different salts, whether its effect is counteracted by the presence in the solution of other bodies not taking part in the reaction, or whether the effect of such bodies may be counteracted by the addition of a greater amount of precipitant, etc., etc., are questions, the answers to which are difficult to find in chemical literature.

With a view to answer, in part at least, these questions, the following work on the precipitation of barium sulphate was undertaken.

A preliminary experiment, which perhaps is worth noting, was first tried:

A solution of 140 cc. water and five cc. concentrated hydrochloric acid was heated nearly to boiling and 0.1984 gram pure recently ignited barium sulphate was added. This was then stirred up and set aside for one hour, when it was filtered and

the barium sulphate washed well with hot water. The filter and the contents were then ignited and weighed, when it was found that ten milligrams of the sulphate had been dissolved. The filtrate was now divided, and to one-half some sulphuric acid was added, and to the other some barium chloride solution. *A precipitate of barium sulphate was produced in both cases.*

Standard solutions of sulphuric acid and barium chloride were now prepared. These were standardized by precipitation from pure water solutions.

The sulphuric acid used in this work was the chemically pure acid of the laboratory, tested for the ordinary impurities.

The barium chloride was recrystallized from the chemically pure salt.

The hydrochloric acid was the chemically pure acid of the laboratory tested for sulphuric acid.

The graduated ware was calibrated and found to be good.

All the precipitates of barium sulphate were ignited by folding up the moist filter, putting into a platinum crucible, "precipitate end" up and so adjusting the flame that the paper would be charred away without letting the crucible become red hot. Finally the heat was raised and the ignition finished. No lid was used on the crucible. By following this plan no reduction to sulphide need be feared.

A number of the precipitates were moistened with sulphuric acid and ignited. No change was noticed.

In the course of the work the following solutions were made:

SULPHURIC ACID SOLUTION.

Solution A.

	cc.	Barium sulphate.
1.	20	0.1978
2.	20	0.1975
3.	20	0.1970
4.	20	0.1978
	Average	0.1970

Solution B.

	cc.	Barium sulphate.
1.	50	0.3277
2.	50	0.3271
3.	50	0.3279
	Average	0.3275

Solution C.

	cc.	Barium sulphate.
1.	5	0.1944
2.	5	0.1940
	Average	0.1942

Solution D.

	cc.	Barium sulphate.
1.	25	0.1544
2.	25	0.1534
3.	25	0.1543
4.	25	0.1538
5.	25	0.1535
6.	25	0.1546
7.	25	0.1539
	Average	0.1542

Rejecting Nos. 2 and 5.

BARIUM CHLORIDE SOLUTIONS.

Solution A.

	cc.	Barium sulphate.
1.	20	0.1181
2.	20	0.1812
3.	20	0.1811
4.	20	0.1792
5.	20	0.1802
	Average	0.1805

Rejecting No. 4.

Solution B.

	cc.	Barium sulphate.
1.	50	0.1985
2.	50	0.1980
3.	50	0.1086
4.	50	0.1985
	Average	0.1984

Solution C.

	cc.	Barium sulphate.
1.	10	0.4004
2.	10	0.4002
3.	10	0.4006
	Average	0.4004

Solution D.

	cc.	Barium sulphate.
1.	10	0.3998
2.	10	0.3994
3.	10	0.3996
	Average	0.3996

Note.—The apparent discrepancies in some of the above averages are to be explained by the fact that before beginning the work the burette used had been very carefully calibrated, and the averages were calculated to correct number of cubic centimeters from the readings as given on the burette. In the course of the work this refinement was found to be wholly unnecessary and was therefore disregarded.

The equation of solutions of sulphuric acid and of barium chloride is: Twenty cc. barium chloride solution = 21.8 cc. sulphuric acid. That is, when mixed in these proportions they will, theoretically, mutually precipitate each other and give 0.1970 gram barium sulphate.

The effect of bringing these two solutions together in this proportion was first tried. The barium chloride solution plus water to make the whole volume up to 140 cc. was heated to boiling and the sulphuric acid run in from the burette.

		Barium sulphate.	Error.
1.	20 cc. $BaCl_2A$+21.8 cc. H_2SO_4A.....	0.1966	—0.0004
2.	20 " " " " "	0.1973	+0.0003
3.	20 " " " " "	0.1979	+0.0009

Solutions of $BaCl_2B$ and H_2SO_4, when brought together in their molecular proportions, weighed as follows:

		Barium sulphate.	Error.
1.	50 cc. $BaCl_2B$+ 30.2 cc. H_2SO_4B.....	0.1979	—0.0005
2.	50 " " " " "	0.1976	—0.0008

These had stood twenty-two hours before filtration, and the results, while not very close, show at least that in water solutions precipitation is practically complete without the presence of an excess of reagent.

A series of precipitations was now made in order to determine the effect of varying quantities of hydrochloric acid upon the precipitation when the two reagents were brought together in their molecular proportions.

The barium chloride solution, water to make the volume up to 140 cc., and the hydrochloric acid were heated to boiling and the sulphuric acid run in cold from the burette.

The same quantities of barium chloride and sulphuric acid were used as above. The time of standing before filtration is

marked over each set. Three precipitations were made with each portion of the hydrochloric acid.

SERIES I.

	1. Five cc. hydrochloric acid. Twenty-five hours. Barium sulphate.	2. Ten cc. hydrochloric acid. Twenty-nine hours. Barium sulphate.	3. Fifteen cc. hydrochloric acid. Thirty-three hours. Barium sulphate.	4. Twenty cc. hydrochloric acid. Forty-four hours. Barium sulphate.
1	0.1908	0.1879	0.1827	0.1875
2	0.1902	0.1870	0.1844	0.1863
3	0.1904	0.1881	0.1838	0.1873

It was thought that after standing twenty-four hours precipitation would be complete and a longer time would have no effect. The results of series No. 4 seem to show differently, however. Accordingly another series was run in which the time of standing was regulated. Otherwise the precipitations were made as above.

These stood twenty-three hours before filtration.

SERIES II.

	1. Five cc. hydrochloric acid. Barium sulphate.	2. Ten cc. hydrochloric acid. Barium sulphate.	3. Fifteen cc. hydrochloric acid. Barium sulphate.
1	0.1902	0.1870	0.1852
2	0.1884	0.1854	0.1849
3	0.1904	0.1846	0.1827

	4. Twenty cc. hydrochloric acid. Barium sulphate.	5. Twenty-five cc. hydrochloric acid. Barium sulphate.	6. Thirty cc. hydrochloric acid. Barium sulphate.
1	0.1832	0.1822	0.1766
2	0.1885	0.1793	0.1833
3	0.1850	0.1789	0.1733

The above results show three things: (1) That less barium sulphate is precipitated in the presence of larger amounts of hydrochloric acid, but this solubility is not proportional to the amount of hydrochloric acid. (2) That the greatest variation of results takes place in the presence of the larger amounts of acid. In other words parallel precipitations don't "check." (3) A much longer time is required to reach the maximum of precipitation in the presence of the larger amounts of hydrochloric acid. See No. 4, Series I.

The effect of a small excess of sulphuric acid was now tried. Three solutions each containing fifty cc. barium chloride *B*, sixty cc. water and twenty cc. hydrochloric acid were heated to boiling and the amounts of sulphuric acid *B*, indicated below, were run in from a burette.

These stood twenty-four hours and weighed as follows:

SERIES III.

				Barium sulphate.	Error.
1.	50 cc. $BaCl_2$ *B*	+ 31.2 cc. H_2SO_4 *B*	= 1 cc. excess	= 0.1839	—0.0145
2.	50 " "	+ 32.2 " "	= 2 " "	= 0.1881	—0.0103
3.	50 " "	+ 33.2 " "	= 3 " "	= 0.1971	—0.0013

The filtrates from the above gave no further precipitate on standing several days.

Another series was run, using five cc. hydrochloric acid instead of twenty cc., but conducted otherwise in the same manner except that they stood from Friday to the following Monday and undoubtedly the maximum of precipitation was reached.

SERIES IV.

				Barium sulphate.	Error.
1.	50 cc. $BaCl_2$ *B*	+ 31.2 cc. H_2SO_4 *B*	= 1 cc. excess	= 0.1951	0.0033
2.	50 " " "	+ 32.2 " " "	= 2 " "	= 0.1963	0.0021
3.	50 " " "	+ 33.2 " " "	= 3 " "	= 0.1964	0.0020

It was now decided to use larger amouuts of sulphuric acid in excess, but in order to hurry matters along, cut down the time of standing before filtration.

In the following series, accordingly, the barium sulphate was filtered off after standing three hours. The whole volume of solution in each case was 150 cc.

SERIES V.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *B*.	No. of cc. in excess of the theoretical am't for precipitation.	Barium sulphate weighed.	Error.
1	50	15	35.2	5	0.1458	0.0526
2	50	15	40.2	10	0.1590	0.0394
3	50	15	45.2	15	0.1688	0.0296
4	50	15	50.2	20	0.1762	0.0222

A steady increase following the larger amounts of sulphuric acid is seen, but it is to be noted that 30.2 cc. sulphuric acid in

three hours did not bring down so large a precipitation as 31.2 cc. sulphuric acid did in twenty-four hours though in the presence of a larger portion of hydrochloric acid. See Series III.

In order to get comparative results the various conditions of the precipitation had to be more carefully regulated. The above results show this very plainly.

Accordingly, the following problem was set: How great an excess of sulphuric acid is required to precipitate completely as sulphate, the barium from fifty cc. of barium chloride *B*, in the presence of five cc. hydrochloric acid in one hour, the whole volume of solution, after adding the sulphuric acid, to be 150 cc.?

Instead of adding a certain number of cc. in excess the sulphuric acid was now measured in equivalents, 30.2 cc. the exact amount to precipitate fifty cc. barium chloride was called one equivalent and different multiples of it were taken.

The barium chloride, water, and hydrochloric acid were heated on the water-bath and the sulphuric acid run in cold from the burette.

SERIES VI.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *B*.	Eqivalents sulphuric acid.	Barium sulphate.	Error.
1	50	5	37.8	1.25	0.1564	0.0420
2	50	5	45.3	1.50	0.1624	0.0360
3	50	5	52.8	1.75	0.1784	0.0200
4	50	5	60.4	2.00	0.1857	0.0127
5	50	5	68.9	2.25	0.1842	0.0142

The fact that No. 5 was lower than No. 4 was referred to the lowering of temperature produced by the addition of the sixty-eight cc. cold sulphuric acid.

The following plan was now adopted:

The sulphuric acid was measured out into beakers and also heated on the water-bath. It was then added to the barium chloride solution, the beakers being washed out three times with hot water, using about four or five cc. each time and the washings also added.

SERIES VII. (Continued from above.)

	Barium chloride *B.* cc.	Hydrochloric acid. cc.	Sulphuric acid *B.*	Equivalents sulphuric acid.	Barium sulphate.	Error.
6	50	5	67.9	2.25	0.1931	—0.0053
7	50	5	75.5	2.50	0.1935	—0.0049
8	50	5	83.0	2.75	0.1956	—0.0028
9	50	5	90.5	3.00	0.1963	—0.0021
10	50	5	39.4	4.00	0.1961	—0.0023
11	50	5	49.2	5.00	0.1962	—0.0022

Note.—The last two results were obtained with a stronger sulphuric acid solution, which was run in cold.

A rapid increase is seen with the first additions of sulphuric acid, the difference becoming less as the sulphuric acid increases.

Another peculiarity was also seen in each one of these series. Although the solutions had been well stirred on bringing the reagents together, had settled clear in a few minutes, and the supernatant liquid had remained clear, yet in running through the filter the filtrates soon became cloudy and a copious precipitate of barium sulphate settled out.

This could be due only to the agitation produced by running through the filter. Later an experiment was tried on this point. Fifty cc. of barium chloride solution, 0.0992 barium sulphate + five cc. hydrochloric acid and water to make the total volume up to 150 cc., was heated in a flask and two equivalents of sulphuric acid added. This was then shaken for ten minutes, allowed to settle for fifty minutes, and then the precipitate was filtered off and weighed.

It gave barium sulphate 0.1979, a minus error of 0.0013 as against an error of —0.0127 in Series VI, with two equivalents.

It seems that in the presence of hydrochloric acid unless there is a sufficient amount of sulphuric acid present to effect complete precipitation, a delicate balance is formed which is affected by a difference in time of standing, in temperature, and amount of agitation on stirring. To avoid adding so large a volume of sulphuric acid solution "*C*" was prepared.

Series VIII was now run. Both solutions were heated on the water-bath and brought together as described above. Solution

in each case was stirred one and one-half minutes and allowed to settle one hour.

SERIES VIII.

	Barium chloride *B*. cc.	Hydrochloric acid. cc.	Sulphuric acid *C*. cc.	Equivalents sulphuric acid.	Barium sulphate.	Error.
1	50	5	20.4	4	0.1971	—0.0013
2	50	5	25.5	5	0.1978	—0.0006
3	50	5	30.6	6	0.1981	—0.0003
4	50	5	35.7	7	0.1980	—0.0004
5	50	5	40.8	8	0.1984	0.0000
6	50	5	45.9	9	0.1985	+0.0001
7	50	5	51.0	10	0.1984	0.0000
8	50	5	56.1	11	0,1985	+0.0001

At last the proper excess to effect complete precipitation under the conditions described above had been found. Seven or eight times the theoretical amount seems necessary. It is to be noted that the change is extremely slow when near the critical point.

A short series was precipitated and weighed, using other solutions, the equation of which was as follows:

Fifty cc. $BaCl_2$, $x = 1$ cc $\pm$ H_2SO_4 $D = 0.1992$ $BaSO_4$.

SERIES IX.

	Barium chloride *x*. cc.	Hydrochloric acid. cc.	Sulphuric acid *D*. cc.	Equivalents sulphuric acid.	Barium sulphate.	Error.
1	50	5	3	3	0.1957	—0.0035
2	50	5	4	4	0.1992	0.0000
3	50	5	5	5	0.1983	—0.0009
3	50	5	5	5	0.1992	0.0000

In this series the sulphuric acid was run in cold.

The maximum amount of precipitate seems to be reached here with less sulphuric acid than when a more dilute solution was used. The same is true of the precipitations made in the presence of ten cc. hydrochloric acid.

Series X was now run, the precipitations being made in exactly the same manner as those of Series VIII, except that ten cc. of hydrochloric acid was put into the solutions instead of five cc.

SERIES X.

	Barium chloride *B.*	Hydrochloric acid.	Sulphuric acid *C.*	Equivalents sulphuric acid.	Barium sulphate.	Error.
	cc.	cc.				
1	50	10	30.6	6	0.1964	—0.0020
2	50	10	35.7	7	0.1974	—0.0010
3	50	10	40.8	8	0.1981	—0.0003
4	50	10	45.9	9	0.1982	—0.0002
3	50	10	40.8	8	0.1970	—0.0014
4	50	10	45.9	9	0.1982	—0.0002

In the presence of ten cc. hydrochloric acid then, a somewhat greater excess of sulphuric acid is required than with five cc. hydrochloric acid.

A short series with the stronger solution gave

SERIES XI.

	Barium chloride *B.*	Hydrochloric acid.	Sulphuric acid *D.*	Equivalents sulphuric acid.	Barium sulphate.	Error.
	cc.	cc.				
1	50	10	5	5	0.1975	—0.0017
2	50	10	6	6	0.1982	—0.0010
3	50	10	7	7	0.1992	0.0000
3	50	10	7	7	0.1991	—0.0001

Series XII. was conducted exactly as Nos. VIII. and X., excepting that fifteen cc. hydrochloric acid was used.

SERIES XII.

	Barium chloride *B.*	Hydrochloric acid.	Sulphuric acid *C.*	Equivalents sulphuric acid.	Barium sulphate.	Error.
	cc.	cc.				
1	50	15	30.6	6	0.1957	—0.0027
2	50	15	35.7	7	0.1955	—0.0029
3	50	15	40.8	8	0.1965	—0.0019
4	50	15	45.9	9	0.1973	—0.0011
5	50	15	51.0	10	0.1972	—0.0012
6	50	15	56.1	11	0.1984	0.0000
7	50	15	61.2	12	0.1983	—0.0001

The point to be noted in this series is that more sulphuric acid is required in the presence of the larger amount of hydrochloric acid.

The other side of the question was now taken up, namely, the precipitation of sulphuric acid with an excess of barium chloride in the presence of hydrochloric acid.

A new difficulty at once presented itself. The old trouble in filtering barium sulphate was experienced. When a small amount of hydrochloric acid was present it was found utterly impossible to do it under the conditions which had previously been followed.

Various experiments were made to avoid this trouble and at last the following scheme was adopted:

The volume was kept at 150 cc. as in the other work. The sulphuric acid, water, and hydrochloric acid were heated on the water-bath and the barium chloride solution, also hot, was added drop by drop with constant stirring. The beakers were then set back on the bath and the solutions stirred at intervals for thirty minutes. They were then set off and stirred at intervals again until cold.

Just before pouring upon the filter the precipitate was stirred up and the filter filled several times. At first a small portion ran through, but this was poured back, and, generally, the rest could be filtered without trouble.

A series was run according to this description, except that the volume was 250 cc.

The exact time of standing before filtering was not noted in this case. It was probably about four or five hours.

SERIES XIII.

	Sulphuric acid *B.*	Hydrochloric acid.	Barium chloride *C.*	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.	cc.			
1	30.2	10	14.9	3	0.1967	—0.0017
2	30.2	10	19.8	4	0.1959	—0.0025
3	30.2	10	14.9	5	0.1965	—0.0019

There was nothing satisfactory to be derived from this series, so Series XIV was run. The volume here was kept down to 150 cc.

SERIES XIV.

	Sulphuric acid *B.*	Hydrochloric acid.	Barium chloride *C.*	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.	cc.			
1	30.2	10	14.9	3	0.1975	—0.0009
2	30.2	10	19.8	4	0.1994	+0.0010
3	30.2	10	24.9	5	0.1983	—0.0001
4	30.2	10	29.8	6	0.2005	+0.0021

Two of these precipitates weigh heavier than theory demands. This could come only from contamination with barium chloride. To test this No's 3 and 4 were transferred to beakers, boiled up with about seventy-five cc. of water and again filtered, ignited, and weighed.

They then gave

3. 0.1980 barium sulphate = —0.0004 error.
4. 0.1987 " " = +0.0003 "

Another series was run in exactly the same manner, except that more care was taken in washing. Each precipitate was washed with boiling water until the filtrate no longer reacted with silver nitrate.

SERIES XV.

	Sulphuric acid *B*. cc.	Hydrochloric acid. cc.	Barium chloride *C*.	Equivalents barium chloride.	Barium sulphate.	Error.
1	30.2	10	9.9	2	0.1965	—0.0019
2	30.2	10	14.9	3	0.1982	—0.0001
3	30.2	10	19.8	4	0.1975	—0.0008
4	30.2	10	24.9	5	0.1988	+0.0004
5	30.2	10	29.8	6	0.1994	+0.0010

No's 4 and 5, on being boiled up with water and reweighed, gave

3. 0.1981 = —0.0003 error.
4. 0.1975 = —0.0009 "

At its best, however, this method of working was unsatisfactory. The precipitate seemed always on the point of running through the filter and indeed traces generally did go through.

The following scheme was accordingly tried in Series XVI.

The volume was kept as before at 150 cc., but thirty cc. of hydrochloric acid instead of ten was put into each solution. The precipitates were not stirred up after being thrown down. In presence of this large excess of acid the precipitates soon became coarse and crystalline and settled rapidly. *No trouble whatever was experienced in filtering them.*

SERIES XVI. (These had stood about four hours.)

	Sulphuric acid *E*.	Hydrochloric acid.	Barium chloride *C*.	Equivalents barium chloride.	Barium sulphate.	Error.
	cc.	cc.				
1	20	30	4.6	1.5	0.0947	—0.0289
2	20	30	6.2	2.0	0.0997	—0.0239
3	20	30	9.3	3.0	0.1114	—0.0122
4	20	30	12.4	4.0	0.1169	—0.0067
5	20	30	15.5	5.0	0.1207	—0.0029
6	20	30	18.6	6.0	0.1192	—0.0044

These filtrates, on standing over night, all showed further precipitates of barium sulphate. The series was accordingly continued, this time the solutions standing about seven hours before being filtered.

The precipitates were crystalline and filtered easily and rapidly and the filtrates, on further standing, showed no traces of barium sulphate.

In spite, however, of the greatest care in washing, it was impossible to get rid of the occluded barium chloride before ignition.

SERIES VII.

	Sulphuric acid *E*.	Hydrochloric acid.	Barium chloride *C*.	Equivl's Barium chloride.	Barium sulphate.	Error.
1	20	30	18.6	6	0.1258	+0.0022
2	20	30	21.7	7	0.1252	+0.0016
3	20	30	24.8	8	0.1268	+0.0032
4	20	30	27.9	9	0.1260	+0.0024

Nos. 2, 3 and 4 were boiled up with water, rewashed, ignited and weighed.

	Barium sulphate.	Error.						
2	0.1236	0.0000	Filtrate	reacted	strongly	with	silver	nitrate.
3	0.1238	+0.0002	"	"	"	"	"	"
4	0.1253	+0.0017	"	"	slightly	"	"	"

No. 4 boiled up the second time 0.1237 $BaSO_4$ = + 0.0001 error. The filtrate in this case reacted strongly with silver nitrate.

To test this boiling up process No. 4 was treated the third time. This time the precipitate weighed 0.1235 and the filtrate did *not* react with silver nitrate.

A last experiment was made to determine the effect of barium

chloride upon the direct solubility of barium sulphate in hydrochloric acid.

0.1248 gram barium sulphate was put in 120 cc. water and thirty cc. hydrochloric acid and beaker marked "*A*."

0.1228 gram barium sulphate was weighed into another beaker with 105 cc. water, thirty cc. hydrochloric acid and fifteen cc. barium chloride *C*. This beaker was marked "*B*."

Both were heated on the water-bath with frequent stirring and then stood over night.

On being filtered and weighed,

"*A*" gave —0.1106 barium sulphate = 0.0142 loss.
"*B*" " —0.1228 " " = 0.000 "

To further test precipitate "*B*" it was boiled up with water as those of Series XVII, and re-weighed. It lost by this operation 0.0002, which is practically nothing.

From the results obtained in this investigation the following conclusions seem justified:

(1) In the precipitation of a barium salt with sulphuric acid in the presence of hydrochloric acid, a very large excess of sulphuric acid is required.

(2) This excess should be greater the greater the amount of hydrochloric acid present in the solution.

(3) It should be greater the shorter the time of standing before filtration. In fact a very great excess seems to effect immediate precipitation.[1]

(4) The greater the excess of sulphuric acid the less stirring seems necessary to bring down the precipitate in a given time.

(5) While barium sulphate obtained by precipitating a barium salt with sulphuric acid in the presence of hydrochloric acid is coarse, crystalline and easily filtered,[1] that obtained by precipitating sulphuric acid with a barium salt in the presence of hydrochloric acid is fine and much disposed to run through the filter unless special precautions are taken.

(6) In general a large excess of barium chloride is required to completely precipitate the sulphuric acid in the presence of hydrochloric acid.

[1] *J. Anal. Appl. Chem.*, 5, 278.

(7) As the hydrochloric acid increases the amount of barium chloride should also be increased.

(8) The greater the amount of hydrochloric acid present the coarser and more crystalline in character is the precipitated barium sulphate. In precipitating in the presence of large amounts of hydrochloric acid the solution should be quite concentrated.

(9) The barium sulphate so obtained, will, however, be contaminated with adhering barium chloride, and no amount of washing before ignition can entirely free it from this occluded chloride. If, after ignition, the precipitate be boiled up with water, again washed, ignited and weighed, and this process be continued until a constant weight is obtained, the sulphate may be entirely freed from the barium salt.

Some subsequent work in this line has shown that heavy precipitates sometimes require three or four treatments before a constant weight is obtained.

(10) Both in the precipitation of barium with sulphuric acid and of sulphuric acid with barium, very concordant results may be obtained if the conditions under which the precipitations are made are similar, but these results may be quite far from correct. A note of this commonplace occurrence in analytical work is made here, because by following the usual method of testing the filtrate for an excess of the precipitating reagent, a strong reaction might be obtained and yet not more than ninety per cent. of the original precipitate be down.

In conclusion I wish to express my thanks to Professor N. W. Lord for helpful suggestions during the course of this work.

DISCUSSION.[1]—T. S. Gladding: I have already shown (see this Journal, **16**, 398; **17**, 181, 397, 772; **18**, 446) that correct results may be obtained if the barium chloride solution be added drop by drop instead of all at once. This is confirmed by Lane (**18**, 682) and is now virtually admitted by Lunge, who precipitates (**18**, 686) by "quick additions (*i. e.*, pouring in the hot barium chloride solution in about ten portions, occupying about half a minute in all, and stirring the mixture all the time, as every chemist would do.)"

[1] Buffalo Meeting, Aug., 1896.

THE ACTUAL ACCURACY OF CHEMICAL ANALYSIS.[1]

By Frederic P. Dewey.

Received July 14, 1896.

THE subject of this paper does not embrace the consideration of ways and means for the increase of analytical accuracy, or the question, what can be or should be attained in that direction. I desire simply to call attention to the degree of accuracy exhibited in actual every day practice. In estimating this, little weight will be given to the evidence afforded by the agreement of duplicate or multiple determinations by the same chemist; for I am convinced that such agreement is a delusion and a snare. Nor will special importance be attached to the agreement of two or even three analysts in special cases, or to the agreement between two methods practiced by the same analyst. I propose to compare the results obtained by several chemists, working upon the same sample and by various methods, in order to exhibit, as I have said, the actual condition of practice.

The available material for illustrating this phase of the question is unfortunately scanty; but something has been done; and I hope, by calling attention to some of the work in this line, to stimulate further work in the same direction by inducing others to prepare suitable samples and submit them to various chemists who are competent and willing to make the necessary determinations and fully describe the methods they employ.

I draw most of my illustrations from the "Transactions of the American Institute of Mining Engineers," the "Proceedings of the Association of Official Agricultural Chemists," and from personal experience.

MANGANESE IN STEEL.

In May, 1881, Mr. William Kent presented a paper to the American Institute of Mining Engineers entitled "Manganese Determinations in Steel,"[2] in which he gave twenty-four determinations of manganese, made by ten different chemists, employing two main methods, on samples from a plate of steel.

[1] Read before the Washington Section of the American Chemical Society, May 14th, 1896, and published jointly with the American Institute of Mining Engineers.

[2] Trans. A. I. M. E., 10, 101.

These results presented the remarkable range of from 1.14 to 0.303 per cent., and one chemist reported results ranging from 1.14 to 0.434 per cent.

A portion of this variation was undoubtedly due to variations in the sample, since the same sample was not used throughout by the different chemists.

Throwing out the anomalous result of 1.14 per cent. we have twenty-three determinations running from 0.619 per cent. to 0.303 per cent., with an average of 0.415 per cent. Thus showing that at that time the determination of manganese in steel, when only about four-tenths per cent. was probably present, might exhibit an extreme variation between the highest and the lowest results of about three-tenths per cent., or seventy-five per cent. of the amount of manganese present.

These results were certainly very discouraging; but if they did nothing else they served to call attention to the very unsatisfactory character of the determination of manganese in steel at that time.

I do not recall any recent symposium on the determination of manganese in this class of material, but in 1886 Capt. A. E. Hunt,[1] in giving a measure of the accuracy of the colorimetric method, speaks of a variation of 0.02 per cent. in steels containing 0.15 to one and five-tenths per cent. of manganese as "sufficiently accurate for all practical work," thus clearly intimating that the current results of analysis by other methods were at least as good. This degree of accuracy, if attained by different chemists upon the same sample, must be considered a satisfactory advance over the results reported by Mr. Kent.

Early in 1883 Mr. G. C. Stone began a series of contributions on the "Determination of Manganese in Spiegel."[2] In his first paper he reported thirteen determinations by five chemists, all working upon the same "works" sample, showing from 15.49 to 13.83 per cent., and also twenty-six determinations by ten chemists, all working upon a sample of the same spiegel, prepared with especial care jointly by Mr. Stone and one of the other chemists, showing from 14.56 to 10.36 per cent. But some of the low results were obtained by experimental methods.

[1] Trans. A. I. M. E., 15, 104.

[2] Trans. A. I. M. E., 11, 323; 12, 295 and 514.

In the fall of 1883 Mr. Stone reported twenty additional determinations by five other chemists, ranging from 14.20 to 10.76 per cent.; the extremes being reported by the same chemist when working by different methods, his favorite method giving from 13.84 to 13.65 per cent., and three low results, less than eleven per cent., being obtained by the Williams' method. In this connection Mr. Stone presented an interesting table, dividing the methods used into four classes and the results into three classes, giving respectively, below thirteen per cent., between thirteen and fourteen per cent., and above fourteen per cent.

In the spring of 1884 Mr. Stone reported twenty-seven new results, nineteen by four new chemists, and eight by one previously reported, whose new results were obtained by several methods.

We have thus seventy-three determinations by nineteen different chemists. Of these two are thrown out on account of the method used, and eleven "because the chemists were not entirely satisfied with them," leaving sixty determinations by eighteen chemists, using twelve methods.

These sixty results range from 14.47 to 12.60 per cent., and average 13.39 per cent. Leaving out eight determinations by one method which is considered to give low results, the lowest determination becomes 12.92 per cent. and the average 13.48 per cent., showing an extreme variation of 1.45 per cent. of manganese between the highest and lowest results, and showing only forty-four per cent. of the results within two-tenths per cent. of the average.

In the discussion of Mr. Stone's second paper, Mr. J. B. Mackintosh[1] presented an analysis of Mr. Stone's first forty-six results, retaining the results by the Williams' method, from which he argued that the evidence pointed to 12.956 per cent. as the true content of manganese in this spiegel. If this is the case, then there is a very decided tendency to get too high results in this class of work.

Taken as a whole, this investigation would seem to show that variations of five-tenths per cent. in the determination of manganese in this grade (ten to fifteen per cent. manganese) of

[1] Trans. A. I. M. E., 12, 300.

spiegel are to be expected, and much wider variations may be found.

PHOSPHORUS IN PIG IRON.

Early in the 80's, Messrs. Potter and Riggs, of St. Louis, Mo., sent out a sample of pig-iron for the determination of phosphorus.

This examination yielded twenty-six results, by eleven chemists, using five methods, ranging from 0.181 to 0.141 per cent., and averaging 0.160 per cent. and showing an extreme variation of 0.040 per cent. The maximum variation reported by any one chemist was 0.017 per cent., while three reported duplicates agreeing with 0.001 per cent. These results have never been published. One of the chemists discovered arsenic in the sample, which would account for some of the variation in the series. His determinations in duplicate were 0.151 and 0.152 per cent.

In February, 1882, Mr. F. E. Bachman presented a paper to the American Institute of Mining Engineers,[1] in which he reported forty-four results by eighteen chemists, using four methods, ranging from 0.165 to 0.096 per cent. and averaging 0.143 per cent. The extreme variation was 0.069 per cent. The maximum variation reported by any one chemist on straight duplicates was 0.01 per cent., and the minimum 0.0004 per cent. Experimental determinations by Mr. Bachman, using different processes, yielded variations amounting to 0.043 per cent.

At the Atlanta meeting in October, 1895, Mr. Geo. Thackray presented a paper, entitled "A Comparison of Recent Phosphorus Determinations in Steel."[2] He first gives a table of determinations of phosphorus by two chemists on eight samples ranging from 0.033 to 0.012 per cent., one chemist uniformly getting high results. One chemist found from 0.080 to 0.074 per cent., and the other 0.110 to 0.088 per cent in these steels. These results were manifestly unsatisfactory.

A second table shows results by three chemists, the buyer's, the seller's and an arbitrator. By the arbitrator's determinations these steels carried from 0.080 to 0.063 per cent. of phosphorus.

[1] Trans. A. I. M. E., 10, 322.
[2] Trans. A. I. M. E., 25, 370.

The maximum difference in any set of three results was 0.017 per cent., and the minimum 0.005 per cent.

These results were obtained in the settlement of sales. As a result of the discussion which accompanied the matter, two samples of steel were prepared and sent to various chemists. A fourth table gives thirty-six results obtained from twenty-three chemists, using twenty-nine methods on one steel, showing results averaging 0.0496 per cent., and ranging from 0.055 to 0.045 per cent., an extreme variation of only 0.010 per cent. Any individual result was practically within 0.005 per cent. of the average.

On the second sample thirty-eight results were reported averaging 0.0835 per cent., and ranging from 0.091 to 0.076 per cent., an extreme variation of 0.015 per cent.

My own results on these steels are not given, as they were not reported in time; but they add two more results by one more chemist in each case, and the results fall within the limits.

These results must be regarded as highly satisfactory, and show that here, at least, is one determination that can be made by many chemists, working in different ways, and yet with results agreeing very closely together. While it may not be necessary to determine many things as closely as phosphorus in steel, yet it would be highly satisfactory if we could do so; and this is a good standard of excellence for us to aim at.

PHOSPHORIC ACID.

As compared with the accuracy secured in the determination of phosphorus in steel, the 1894 report of the Association of Official Agricultural Chemists,[1] shows that on one sample thirty-nine determinations of insoluble phosphoric acid by eighteen chemists, working by the official method, showed results ranging from 0.45 to 0.03 per cent., with an average of 0.27 per cent., the extreme variation being 0.42 per cent., or over one and one-half times the average determination.

By another method, on the same sample, thirty-six determinations by nineteen chemists showed results varying from 0.34 to

[1] Proceedings of the Eleventh Annual Convention of the Association of Official Agricultural Chemists, August 23, 24, 25, 1894. Bulletin 43, U. S. Department of Agriculture, Division of Chemistry, p. 76.

0.04 per cent., with an average of 0.19 per cent., the extreme variation being 0.30 per cent., or over one and one-half times the average.

We have thus seventy-five determinations by nineteen chemists working by two methods, showing results ranging from 0.45 to 0.03 per cent., with an average of 0.233 per cent., the extreme variation being 0.42 per cent., or nearly twice the average determination.

On another sample thirty-three determinations by seventeen chemists working by the official method, showed results ranging from 3.85 to 2.24 per cent., with an average of 2.82 per cent., the extreme variation being 1.61 per cent., or considerably more than one-half of the average.

By another method, on the same sample, thirty-five determinations by seventeen chemists showed results ranging from 3.49 to 2.18 per cent., with an average of 2.83 per cent., the extreme variation being 1.31 per cent., or nearly one-half the average.

Summing up again, we have sixty-eight determinations by eighteen chemists working by two methods, showing results ranging from 3.85 to 2.18 per cent., with an average of 2.82 per cent., the extreme variation being 1.67 per cent.

The same report[1] shows that on one sample the results of twenty-nine determinations of citrate soluble phosphoric acid by fourteen chemists, by the direct method of Ross, varied from 2.47 to 1.04 per cent., with an average of 1.52 per cent., the extreme variation being 1.43 per cent., or nearly equal to the average of all the determinations.

On the same sample, by the official method, the results of twenty-three determinations by fourteen chemists ranged from 2.26 to 1.18 per cent., with an average of 1.46 per cent., the extreme variation being 1.08 per cent., or over two-thirds of the average determination.

Summing up, we have fifty-two determinations by fourteen chemists working by two methods, ranging from 2.47 to 1.04 per cent., and averaging 1.49 per cent., the extreme variation being 1.43 per cent., or nearly equal to the average.

[1] *Ibid.*, p. 72.

On another sample thirty-six determinations by fifteen chemists by the direct method of Ross, range from 3.29 to 1.87 per cent., with an average of 2.36 per cent., the extreme variation being 1.42 per cent., or considerably over one-half of the average determination.

On the same sample, twenty-four determinations by fifteen chemists, ranged from 3.40 to 2.08 per cent., with an average of 2.60 per cent., the extreme variation being 1.32 per cent., or a little over one-half of the average determination.

Summing up, we have sixty determinations by fifteen chemists working by two methods, ranging from 3.40 to 2.08 per cent., and averaging 2.44 per cent., the extreme variation being 1.32 per cent., or a little over one-half of the average determinations.

In the determination of the total phosphoric acid,[1] forty-five determinations, by eighteen chemists, ranged from 20.67 to 19.74 per cent., with an average of 20.09 per cent., the extreme variation being 0.93 per cent. By a volumetric method, thirty determinations, by eleven chemists, ranged from 20.60 to 19.83 per cent., with an average of 20.14 per cent., the extreme variation being 0.77 per cent. By another volumetric method, twenty-one determinations by ten chemists, ranged from 20.45 to 19.27 per cent., with an average of 19.96 per cent., the extreme variation being 1.18 per cent.

Combining these results, we have ninety-six determinations by eighteen chemists working by three methods, ranging from 20.67 to 19.27 per cent., with an average of 20.08 per cent., the extreme variation being 1.40 per cent.

Similarly, on another sample, we have 120 determinations, by twenty-two chemists, working by the same three methods, ranging from 18.15 to 16.25 per cent., with an average of 17.26 per cent., the extreme variation being 1.90.

Again, on another sample, we have ninety-six determinations by twenty-one chemists, working by the same three methods, ranging from 2.85 to 2.20 per cent., with an average of 2.50 per cent., the extreme variation being 0.65 per cent.

COPPER.

At the August meeting of the A. I. M. E., in 1882, Mr. W.

[1] *Ibid.*, pp. 81, 82, 83.

E. C. Eustis presented a paper entitled "Comparison of Various Methods of Copper Analysis."[1] For the purpose of this comparison a very complex sample was made up, containing sulphides, oxides and metallic copper, a silicate, sulphides of iron and zinc, arsenic and nickel. The paper reports forty-five determinations by seventeen chemists, using some eight methods. The results showed a wide variation, ranging from 53.34 to 43.92 per cent. and averaging 47.75 per cent. On throwing out a set of six results from one concern, all of which were more than two per cent. and two of them nearly five per cent. above the nearest other result, as being manifestly too high, and two results by one chemist and one method, which were more than two per cent. below the nearest other result, the series still ranges from 48.72 to 46.24 per cent., with an average of 47.23 per cent., and a maximum variation of 2.48 per cent., which cannot be considered very satisfactory.

The same paper reported seventeen determinations by seven chemists on borings of pig copper. These ranged from 91.07 to 98.17 per cent. and averaged 94.25 per cent. On throwing out two results that were nearly three per cent. higher than the nearest other result, and four that were over three per cent. below the nearest other result, the series ranges from 94.91 to 94.38 per cent. with an average of 94.69 per cent. The extreme variation of only 0.53 per cent. must be regarded as very good work, especially when we consider the character of the material.

At the Florida meeting in March, 1895, the results of a symposium on copper and copper matte, initiated by Dr. A. R. Ledoux, of New York City, were presented.[2] Eight chemists reported the copper in the matte, some in duplicate or more, as determined by electrolysis, as ranging from 55.17 to 54.50 per cent. and averaging 54.91 per cent. The extreme variation was only 0.67 per cent; and this must be regarded as satisfactory, and very much better than the results on Mr. Eustis' complex mixture.

Six chemists reported results by the cyanide method, ranging from 54.8 to 50.55 per cent, all but one of the results being below

[1] Trans. A. I. M. E., 11, 120.

[2] Trans. A. I. M. E., 25, 250 and 1000.

the lowest electrolytic result. These cannot be regarded as satisfactory.

A plate of copper made from melted anodes was drilled and six chemists reported the copper in the drillings, as found by the electrolytic method, as ranging from 98.46 to 97.04 per cent., and averaging 97.67 per cent. with a maximum difference of 1.42 per cent. These results are not as good as those previously reported by Mr. Eustis.

GOLD AND SILVER IN COPPER MATERIALS.

The symposium above referred to was undertaken primarily to test methods of assaying copper material for gold and silver. Fourteen chemists reported the silver by scorification assay, some entirely uncorrected, some partially corrected, and some corrected for both loss in slag and cupel and presence of copper in the silver button. The averaged results ranged from 135.38 to 122.88 ounces per ton and averaged 128.86 ounces per ton; the extreme variation being 12.5 ounces per ton, or nine and seven-tenths per cent. of the average.

Nine chemists reported ten results by combined wet and scorification methods, a few of them corrected for slag and cupel absorption. The averaged results ranged from 130.68 to 123.03 and averaged 127.25 ounces per ton. The extreme variation was seven and six-tenths ounces per ton, or 5.97 per cent. of the average determination.

One chemist reported 123.6 ounces per ton by crucible method.

Another reported 126.2 ounces per ton by combined wet and crucible method, corrected for slag and cupel.

Summing up, we have twenty-six results by twenty chemists working by two main methods, but both of them modified in various ways, and two methods, each by a single chemist, varying from 135.38 to 122.88 and averaging 127.94 ounces per ton. The extreme variation was 12.5 ounces per ton, or 9.77 per cent. of the average determination.

In the case of the silver assay of the copper borings, nine chemists reported by the scorification method, with and without corrections. The averaged results varied from 164.35 to 154.40, and averaged 159.36 ounces per ton. The extreme variation was 9.95 ounces per ton, or 6.24 per cent. of the average.

Fifteen chemists reported sixteen results by combined wet and scorification methods, with and without corrections. The averaged results varied from 161.40 to 148.50 and averaged 156.48 ounces per ton. The extreme variation was 13.9 ounces per ton, or 8.88 per cent. of the average. A single chemist reported 161.35 ounces per ton by combined wet and crucible process, corrected for slag and cupel.

Summing up, we have twenty-six determinations by twenty chemists working by three methods, ranging from 164.35 to 148.5 and averaging 157.67 ounces per ton. The extreme variation was 15.85 ounces per ton, or 10.05 per cent. of the average determination.

Twenty chemists working by the four methods reported twenty-six results on the gold in the matte varying from 2.41 to 1.85 and averaging 2.245 ounces per ton. The extreme variation was 0.56 ounce per ton, or 24.94 per cent. of the average.

On the gold in the copper borings twenty chemists working by two main methods, each one variously modified, and the combined wet and crucible method by a single chemist, reported twenty-six results varying from 0.501 to 0.205 and averaging 0.307 ounce per ton. The extreme variation was 0.296 ounce per ton, or 96.4 per cent. of the average determination.

POTASH.

In the determination of potash the 1894 report of the Association of Official Agricultural Chemists[1] gives six determinations of potassium chloride by six chemists by one method, ranging from 97.79 to 99.32 per cent. with an average of 98.56 per cent, the extreme variation being 1.53 per cent. By another method on the same sample seven determinations by seven chemists range from 97.21 to 98.86 per cent., averaging 98.16 per cent. Combining these results we have thirteen results by seven chemists, by two methods, ranging from 97.21 to 99.32 per cent. and averaging 98.35 per cent., the extreme variation being 2.11 per cent.

This report contains also a table of results on soil analyses[2] which I quote entire.

[1] page 22.
[2] page 41.

TABLE OF AVERAGES.

Soil Sample No. 2.

	Provisional method.					Hilgard method.				
	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.
		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.	
Insoluble matter	14	76·874	77·733	76·19	2	12	76·619	77·910	75·380	3·3
K_2O	13	0·405	0·510	0·27	59	11	0·431	0·670	0·250	98
CaO	13	0·460	0·605	0·360	53	10	0·538	0·680	0·390	54
MgO	11	0·425	0·589	0·360	54	9	0·425	0·627	0·320	72
Fe_2O_3	9	3·504	4·260	2·955	37	7	4·347	6·400	3·300	70
Al_2O_3	9	6·613	7·500	6·240	19	7	6·285	6·828	4·460	38
P_2O_5	16	0·496	0·600	0·410	38	12	0·510	0·660	0·430	45
Fe_2O_3, Al_2O_3, and P_2O_5 ...	12	10·754	11·400	10·220	11	10	11·071	12·100	10·550	14
N	7	0·276	0·290	0·262	10	..	.....	.....	.....	....
P_2O_5, Goss method	5	0·467	0·493	0·425	15	..	.....	.....	.....	....

Soil Sample No. 3.

	Provisional method.					Hilgard method.				
	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.	No. included.	Average.	Highest.	Lowest.	Difference in per cent. of average.
		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.	
Insoluble matter	11	80·520	81·255	79·980	1·6	10	80·448	82·010	79·47	3·1
K_2O	10	0·422	0·500	0·305	46	9	0·396	0·630	0·240	98
CaO	9	0·372	0·425	0·300	33	8	0·411	0·600	0·275	79
MgO	8	0·381	0·524	0·270	67	7	0·369	0·490	0·265	61
Fe_2O_3	6	3·251	4·330	2·310	62	5	3·746	4·870	3·025	49
Al_2O_3	6	6·191	7·440	5·670	29	5	5·770	6·164	5·050	19
P_2O_5	11	0·418	0·555	0·350	49	9	0·429	0·560	0·309	59
Fe_2O_3, Al_2O_3, and P_2O_5 ..	8	9·927	10·350	9·440	9	7	10·091	10·590	9·550	10
N	6	0·190	0·224	0·175	26	..	.....	.....	.....	....
P_2O_5, Goss method	4	0·369	0·390	0·354	10	..	.....	.....	.....	....

REVIEW.

ON THE DEVELOPMENT OF SMOKELESS POWDER.[1]

By Charles E. Munroe.

To intelligently present a sketch of what has been done in the development of smokeless powder, it is necessary to first briefly review the history of black gunpowder. Although the place and date of its origin and the name of its inventor are yet open to dispute, it is generally accepted that it was employed as a propellent in cannon at the battle of Crécy in 1346, and in small arms for some time prior to this date, and that it then consisted of a mixture of niter, charcoal and sulphur. Considering the existing state of chemistry, it is fair to infer that the making of gunpowder, like the manufacture of guns, was for long an empiric art, and that, notwithstanding that Tartaglia, Galileo, Newton, Huygens, and many others speculated upon and discussed the effects which gunpowder produced upon projectiles; that granulating was employed in 1445; that Cellini had observed the necessity of adapting the grains to the piece; that sizing was practised in France in 1525, and that Hawksbee had in 1702 measured the volume of gas resulting from a known volume of gunpowder, the science of gunnery had no existence until Robins devised the ballistic pendulum by which he measured the velocity of projectiles and with which he obtained the experimental data upon which his "New Principles of Gunnery," printed in 1742, was founded. The science of exterior ballistic was materially improved when Hutton, in 1778, extended Robins' principle to the use of the gun as the pendulum also, for it became then possible to not only measure the velocity of the projectile, but the energy involved in the reaction, and this method was employed for larger and larger calibers until it reached its practical limit in the very elaborate and precise series of experiments made at the arsenal in this city (Washington) from 1842 to 1847, by Major Mordecai, who succeeded in swinging cannon weighing about 7,700 pounds and throwing 32-pound balls; but this necessitated the use of a pendulum weighing over 9,300 pounds, the center of gravity of which was over fourteen feet below the axis of suspension. The weight and length of the pendulum increases so rapidly with the increase of the projectile that to determine by this method the velocity of the projectile from a 100-ton gun, would require towers like those from which the Brooklyn bridge is suspended, between which to swing the pendulum.

[1] Presidential addrees delivered before the Washington Section of the American Chemical Society, Feb. 21, 1896.

Opportunely as this limit was approached, Dr. Joseph Henry announced, in 1843, his invention of a method for the determination of velocities by interposing screens, which were electrically connected with chronographs, in the path of a projectile and at definitely determined distances from the gun, and this method, which while possessing the merit of great simplicity, is at the same time very precise and capable of being used for determining the velocities of projectiles from guns of every calibre, is now universally employed with chronographs, such as the Boulengé, Schultz-Deprez, and Mahieu, while the principle has been extended by Captain Noble to the study of interior ballistics, in his very ingenious chronoscope by which the velocity of the projectile can be determined at frequent intervals, even when it is moving through the bore of the gun.

The ability to measure the velocities which it produced led to active investigations into the properties of gunpowder and resulted in the experiments of Lavoisier, between 1777 and 1778 on the deflagration of powder, of Berthollet, on the best proportions for mixing the ingredients, of Gay Lussac, on the refining of niter, of Violette, on the production, composition and properties of charcoal, of Gay Lussac and Chevreul, of Bunsen and Schischkoff, of Linck, and of Kâroyli, on the composition and volume of the products of the combustion of this substance, and of many other experimenters on the effects resulting from differences in the density, hardness, size of grain and other physical characteristics of the explosive. But notwithstanding the great advance made through the invention of methods by which to measure the velocity of the projectile and the recoil of the piece, the science of gunnery was still incomplete without an accurate knowledge of what was going on within the chamber and particularly what pressures were produced and how this pressure was distributed within the gun before the projectile left its seat and while it was traveling through the chase; yet, although direct experimental determinations of the pressure exerted by fired gunpowder were made by Count Rumford in 1797 in a somewhat rude device, and numerous indirect estimations were deduced from the observations of Robins on the volume of the gases produced by its combustion and from the more precise and detailed researches of Bunsen and Schischkoff and the other experimenters previously referred to, no practical means were at command by which to make direct measurements of the pressure developed within the gun itself until Captain Rodman, in 1857, invented the pressure gauge, described in his "Reports of Experiments," published in Boston, in 1861, which in common with several modifications of it, such as the Noble

crusher gauge and the Woodbridge spiral gauge, came into general use in all experimental firing and in the proving of guns and powders.

In estimating the pressure developed by powder from the data obtained in their chemical analyses of its products, Bunsen and Schischkoff proceeded on the assumption that Piobert's conclusion from his experiments, *viz.*, "that the rate of combustion of powder is not affected to any sensible degree by heat or pressure," was correct; but their conclusions having been questioned by many authorities, among them by Vignotti, in 1861, and by Craig about the same time, who showed that the products of combustion differs with the pressure, and their physical data by F. A. P. Barnard, who submitted them to a reinvestigation in 1863, and arrived at a widely different result; and they having also failed of verification by the pressure gauge, the matter was again experimentally attacked by Noble and Abel, who employed as a firing chamber a hermetically closed steel cylinder sufficiently strong to resist rupture by the explosion of a charge of powder which completely filled it (such as Dr. Woodbridge had previously used at the Washington navy yard in 1856), in which pressure gauges were enclosed, and they fired the charge by the electric method invented by Dr. Robert Hare in 1832. In addition the apparatus was so contrived that the gaseous and solid products could be collected, measured and analyzed at will.

With this they found that when powder is fired in a confined space the products of combustion are about fifty-seven per cent. by weight of ultimately solid matter, and forty-three of gases, which at 0° C. and 760 mm., occupy about 280 times the volume of the original powder. That the temperature of explosion is about 2,200° C., and the tension of the products, when the powder entirely fills the space in which it is fired, is about 6,400 atmospheres, or forty-two tons per square inch.

When fired in the bore of the gun it was shown that the work on the projectile is effected by the elastic force resident in the permanent gases, but the reduction of temperature, due to the expansion of the permanent gases, is in a great measure compensated for by the heat stored up in the liquid residue. The total theoretical work of gunpowder when expanded indefinitely (as for instance in a gun of infinite length) was deduced from the data which they accumulated as about 486 foot tons per pound of powder.

They further ascertained that the fine grain powders furnish decidedly smaller portions of gaseous products than large grain or cannon powders; that the variations in the composition of

the products of explosion, in a closed vessel, furnished by one and the same powder, under different conditions as regards pressure, and by two powders of similar composition, under the same conditions of pressure, are so considerable that no chemical expression can be given for the metamorphosis of a gunpowder of a normal composition, and that the proportions of the several constituents of the solid residue are quite as much affected by slight accidental conditions of explosion of one and the same powder in different experiments as by decided differences in the composition or in the size of the grain.

The subsequent researches of Berthelot and Vieille, and of Sarrau and Vieille showed that gunpowder was not singular in that its combustion products varied with the variations in the conditions prevailing in the firing chamber, but that this same rule held for gun cotton, picrates and other explosives, also, and that consequently the chemical reaction taking place and the physical phenomena attending them were changed with these varying conditions, and more particularly with variations in the density of loading.

Before the invention of the instruments of precision above alluded to, guns were constructed largely on principles deduced from observations of exterior phenomena, and powder was manufactured largely by rule of thumb. With the ability to determine quantitatively their behavior, each has been studied in a scientific manner and improved by rational methods.

By their use the real importance of uniformity in chemical and physical composition was demonstrated for the powder, and the means by which to "prove powder" before issue were supplied, while rational blending, by which to minimize the irregularities incident to the best commercial processes was made possible. At the same time greater uniformity in granulation was secured; the best form of grain was developed for great guns through the pebble to the mammoth, disk, pellet, sphere, cylinder, hollow cylinder, hexagon and cube to the hexagonal prism, with one canal, which is now generally adopted, and which is a modified form of the grain invented by Rodman; the size of the grain best adapted for a given gun was ascertained, and the size rose trom one-sixth of an inch, as used in the 15-inch S. B., to fhe hexagonal prism one inch in height by 1.36 inches in diameter; the density of the grain rose from 1.60 to 1.86; the effect of prearranged variations of density in grains, as proposed by Doremus and carried out in the Fossano powder, was determined; and the important part which moisture played in the reactions going on in the chamber with the necessity for introducing it into the grain in definite quantities and retaining it there

within very narrow limits was discovered. In fact these methods of inspection have become so precise and the powder specifications so severe that the manufacture of military gunpowder is now a most difficult art, and the maker must not only watch the barometer and thermometer and hygrometer to determine his action at each step of his process, but according to one authority, he must "vary his treatment with each passing cloud," and notwithstanding all precautions, it is no uncommon thing for the best makers to have their product rejected at the proving ground.

Besides these improvements in black gunpowder, which have resulted from our ability to accurately gauge its performance, these instruments have shown us that it is possible to avail ourselves of the energy stored up in underburned charcoal or carbohydrates if we but modify the brusqueness incident to mixtures containing them by adopting the proper size, form, hardness and density for the grain, and this has resulted in the cocoa or brown prismatic powders which have come into very extented use since 1880.

The valuable properties of the compressed powder were then applied for use in small calibers and enabled Hebler to realize a marked increase in efficiency for his rifles, and in these forms the limit of efficiency of gunpowder appeared to be reached.

But while this was being accomplished, progress was being rapidly made along other lines which we will briefly point out.

Among the other inventions in gunnery which preceded the invention of smokeless powder, and made its use possible or essential, we may mention the introduction of rifling, by which greater accuracy of fire and a higher velocity and penetrating effect is obtained, and which, while invented by Gaspard Zollner, of Vienna, in 1480, did not come into vogue until 1830, or general use until much later. Breech loading, which was known among the Chinese as early as 1313, but which has practically been developed since 1863, our civil war having been fought chiefly with muzzle loaders. Percussion caps, invented by Joseph Egg, in 1818, and adopted, with the nipple, in France in 1838. Self obturating metallic ammunition, which depended on the preceding invention, and which we owe apparently to Flobert, who introduced it for use, with a quick powder, in his parlor rifle in 1845, though it did not come into use for larger caliber for some years later, and then only after the discovery of a metal having the necessary ductility and strength from which to strike the shells and the perfecting of machinery for their economic and rapid production. Magazine rifles and machine guns, the earlier practical forms of the latter being the weapon

exhibited by Dr. Gatling in 1867, and the French mitrailleuse, and which have now developed into the automatic machine guns, such as Maxim, Colt, Hotchkiss, and others possessing an almost incredible rapidity of discharge. Rapid fire large caliber guns, which, like the foregoing, depend for their development on the prior invention of the breech mechanism, and the metallic ammunition and which have reached calibers of six-inch diameter and throw 100-pound shot at the rate of six per minute, with a velocity of over 2,000 feet per second. Breech-loading, built-up steel rifles, which, while embodying the ideas of a gun of equal strength, as announced by Professor Treadwell, in 1843, the mechanical devices of Chambers patented in 1849, and the principles of initial tension, as expounded in Rodman's publication of the same year, have been developed, at least in this country, only since the appointment of the Gun Foundry Board by Secretary Chandler, and whose manufacture was then rendered possible only through the perfection which our machine tools had attained and the improvements achieved in the metallurgy of steel. Small caliber rifles, with steel or german-silver mantled bullets, which are sighted for about two miles, and whose projectile will pierce six men, standing one behind the other in close order, at 1,000 yards. And finally to the invention of range-finders or telemeters, through which by trigonometric or mechanical methods, the position of the far distant targets now in range of new weapons may be located with precision.

For it is evident that to use these precise and powerful weapons and instruments, with the accuracy and rapidity they are capable of, the atmosphere must remain clear, and the piece must remain clean, while at the same time the highest attainable velocity must be imparted to the projectile without an undue strain being brought upon the gun. Yet we have seen that Noble and Abel found that military gunpowder gives off, on combustion, fifty-seven per cent. by weight of ultimately solid matter which is either thrown into the atmosphere to produce smoke or left as a residue to foul the bore. How considerable this smoke producing capacity of gunpowder is may be estimated if we take a Gatling firing 1200 rounds of small arm ammunition per minute (and this by no means expresses the highest attainable speed to-day) and assume that all the solid matter is driven out the gun, when we shall find that each minute six and six-tenth pounds of finely divided solid matter will be projected into the atmosphere. Add to this, in a general engagement, the smoke from the great guns, which, as with the 110-ton gun, can project 528 pounds of this solid product at each discharge, and that coming from the rapid

fire, and magazine rifles, and it is obvious that unless a favorable breeze is blowing or other favorable atmospheric conditions prevail, the force or ship will soon be enveloped in an opaque cloud of smoke and be at the mercy of an invisible foe. It is, I repeat, conditions such as these which have rendered smokeless powder, of good ballistic qualities, a great desideration, if not an absolute necessity.

While the development of the projectile, the musket, the machine gun, and ordnance; the perfection in the compositions, forms, and manufacture of gunpowder; and the invention of the instruments and devices for gauging and controlling their performance was going on, chemists were engaged in adding their contributions to the fund of human knowledge in the field of explosives. In 1788 Hausmann discovered "picric acid," in 1800 Howard discovered mercuric fulminate, in 1845 Schönbein discovered gun cotton, in 1845 Sobrero discovered nitroglycerin, in 1875 Nobel invented explosive gelatine, and in the meantime, or subsequently, numerous allied nitro-substitution compounds, nitric ethers and diazo-bodies, less generally known than those above enumerated, were produced, and identified, and shown to possess explosive properties.

The earlier experimental tests of these bodies proved that not only were some of them more powerful or more violent explosives than gunpowder, but that no smoke accompanied their explosion, since the products of their explosive decomposition were gases or vapors at the prevailing temperatures and efforts were put forth soon after their discovery to adapt them for use as propellents. These, together with various organic solids, and liquids to serve as solvents and hardening agents and ammonium and barium nitrates to serve as oxidizing agents were known and at hand.

The earliest experiment with smokeless powder was probably that made by Howard, in 1800, when he tested the properties of his newly discovered mercuric fulminate and found that though this violent agent produced little smoke, imparted a low velocity to the projectile and but a slight recoil to the piece, it burst the chamber, and demonstrated its unfitness to compete with gunpowder as a ballistic agent. Nevertheless this substance has since found a limited use, when mixed with solid diluents which act as restrainers, in ammunition for parlor rifles, and it is noticeable that when firing this ammunition there is little smoke and a scarcely audible report attending the discharge.

In 1806 Grindel carried out a somewhat extended series of experiments with a view to substituting ammonium nitrate for potassium nitrate as the oxidizing agent in gunpowder mix-

tures but the deliquescent character of the ammonium salt rendered the powder made with it useless under the then existing conditions, and has proven a formidable obstacle to its use in many of the attempts subsequently made. The fact, however, that the products of its combustion, at the prevailing temperature, are wholly gaseous rendered it a tempting material to inventors of smokeless powders and it has been more recently used, among others, by F. Gaens, who, in 1885, patented, in Germany, his so-called "Amide Powder," produced by mixing eighty parts of ammonium nitrate and 101 parts of potassium nitrate, with forty parts of charcoal. He claimed that this mixture was not hygroscopic and was practically smokeless, and he held that by the reaction consequent on the ignition, a potassamine was formed which was both volatile and explosive. Whatever the nature of the reaction, it appears from the reports that an ammonium nitrate powder was produced about this time in Germany and later in England, under the name of Chilworth Special, which possessed remarkable ballistic properties and yielded comparatively little smoke, which speedily dispersed, and which bore exposure very well until the humidity of the atmosphere approached saturation.

It is possible that the ammonium nitrate used may have been produced by Benker's process, in which the salt is formed by metathesis from solutions of sodium nitrate and ammonium sulphate exposed to a temperature of $-15°$, or below, for it is claimed that the ammonium nitrate which crystallizes out under these circumstances is of extraordinary purity and not at all hygroscopic.

It would appear that though these ammonium nitrate powders are slightly hygroscopic, they may retain their good qualities for long times in the hermetically sealed cases used in fixed ammunition up to the six-inch rapid fire gun, but that we know that the small amount of water necessarily present produces marked changes during long periods of storage with varying temperatures and that the ammoniacal salts attack the copper of the shells. Besides, too, we must remember that ammonium nitrate in common with other ammonium salts gives off ammonia, when heated or exposed to the air, and becomes acid so that we are debarred from using it in the presence of any bodies affected by the acid.

The next step toward the development of our modern smokeless powder was taken when, soon after the discovery of guncotton, in 1845, attempts were made to use this material as a propellent. These experiments were made in Germany, France, and England, and a very extended series were carried on by

Major Mordecai, at the Washington Arsenal, but the material, owing to its form and the imperfection in its manufacture, proved too brisant and too irregular in its action, and so unstable on keeping as to undergo decomposition in storage. The material having been proved to possess many valuable qualities was not wholly abandoned, but it continued to be the subject of study by many chemists until in 1862, it seeming that Baron von Lenck had so perfected the methods for its manufacture and purification as to ensure stability and uniformity of composition. Austria adopted it as a propellent and supplied thirty howitzer batteries with guncotton cartridges.

This is the first instance in which a really smokeless powder was employed on any but an experimental scale and this powder foreshadowed in its composition and many of its characteristics, the best modern powders of the smokeless class. The guncotton as then made retained the fibrous condition of the original cotton and in the Austrian cartridges it was spun into thread and woven into circular webs like lamp wicks, or braided, or wound on wooden or paper bobbins, and so arranged in the piece as to secure the desired air spacing as well as to insure ignition from the front. As thus used, it was claimed to be uninjured by dampness; to require a charge of but one-fourth to one-third of that of the powder previously employed; to be capable of being regulated so as to produce widely varying effects at will; to leave no residue to foul the piece; and to produce no smoke, while the gases evolved were less injurious to both the piece and men serving it than those of gunpowder. At the same time it produced less heating effect on the gun.

Unfortunately, about this time, the factory at Hirtenberg, where the guncotton was made, blew up for some undiscovered cause, and accidents having occurred with the guns, the use of guncotton was abandoned by the Austrians.

Its fate seemed now to be sealed, but such was not the case, for the scene of action then passed to England, where Abel not long after succeeded in effecting a more complete purification of the body by pulping it prior to the final washing processes, thus cutting the tubular fiber into short lengths and rendering it possible to remove the last traces of acid retained within the tubes by capillarity and which had been the occasion of its decomposition with time. Having thus obtained his pulped, purified guncotton he compressed it into such forms as was desired, and in 1867 and 1868 he obtained with it some very promising results when used with field guns. But although comparatively small charges often gave high velocities of projection without any indications of injury to the gun, the uniform fulfillment of the

conditions essential to safety proved then to be beyond control, and the military authorities not being, at that time, alive to the advantages that might accrue from the employment of a smokeless explosive in artillery, experiments were discontinued not to be resumed for nearly twenty years, and use was found for compressed guncotton in military and naval mining and especially in filling torpedoes, where it has been found the most efficient and satisfactory explosive thus far applied to this purpose.

But sportsmen, to meet whose wants and wishes many noteworthy improvements have been made in the arts, did appreciate the value, to marksmen, of smokelessness combined with high velocities and absence of fouling, and the progress made during the succeeding twenty years in the adaptation of organic nitrates to use as propellents was under their patronage and in response to their demands, and naturally, the first object sought was to so restrain the violence of the explosive that rupturing explosions, such as had occurred, could not be induced under the conditions in which the powder was to be used.

One of the first to realize a considerable degree of success was Captain Schultze, of the German artillery, who made a powder from well purified and partly nitrated wood. For this purpose he sawed the wood into sheets about one-sixteenth of an inch in thickness, which were passed through a machine that punched out discs or grains of uniform size. The grains were then deprived of their resinous matter by being boiled in sodium carbonate, washed, steamed, and then bleached with chloride of lime, when finally, after drying, the cellulose was nitrated in an acid mixture, such as is used for making guncotton. The nitrated wood was then steeped in a solution of potassium and barium nitrates, and when dry the powder was finished. By this means a nitrocellulose was produced which was diluted with unconverted cellulose and metallic nitrates, which were so intimately mingled that a fairly even rate of combustion was obtained though abnormal results were not wholly avoided.

The advantage of using nitrates and combustible organic substances as diluents was soon recognized ; and, as a consequence, many powders of this nature were devised, some thirty of them having been produced and many of these put on the market, in which we find that potassium, sodium and barium nitrates, and potassium chlorate were used as oxidizing agents and sugar, cellulose, charcoal, sulphur, starch, dextrin, gums, resins, and paraffine as combustible diluents and cementing agents. All, however, approximated black gunpowder, as regards physical

structure and none attained to complete success as regards uniformity of fire and reliability of pressure.

In 1882 Messrs. Reid and Johnson patented the process for making E. C. powder, in which the pulped nitrocellulose and nitrates was agglomerated into grains by revolving the moistened mass in barrels, drying the grains, moistening with ether to harden them, and then coloring them with aurine.

About 1885 Messrs. Johnson and Borland produced the J. B. powder, in which a new idea, as regards powder manufacture, was introduced, though it had been used elsewhere for many years. The inventors mixed nitro cotton with barium nitrate and with or without charcoal or torrefied starch and granulated the mixture in a revolving drum, while the water was admitted in a fine spray. When granulated the grains were dried and then moistened with a solution of camphor in petroleum spirit, and after a time heated in a water jacketed vessel to evaporate the benzine, and the bulk of the camphor. By this treatment the grains were hardened and rendered more slowly inflamable.

As this method of treatment resembles in some particulars that followed in the production of celluloid, though it differs in details, and as several of the smokeless powders are made by methods which are adapted from this art, you will pardon me if I briefly describe it.

Celluloid is made from that form of cellulose nitrate known as nitro-cotton or soluble guncotton, and which is produced by immersing unsized and uncalendered tissue paper for a short time in a comparatively weak acid, both being kept at a moderately high temperature. This nitro-cotton is pulped in a rag engine, dried and moistened with camphor spirits. If a considerable portion of camphor spirits be added, and the mixture be allowed to stand for awhile, the mass becomes converted into a soft translucent amber gum; with more of the spirit the nitro-cotton will be completely dissolved; but as carried out, the proportion of spirit added is insufficient to produce a very apparent change.

The mixture is now taken to incorporating rolls or "grinders," (as they are called in the caoutchouc industry), where it is intimately mixed and well pressed; when the particles cohere and the whole becomes converted into a plastic, translucent homogeneous mass which behaves like India rubber and resembles it superficially in every particular but color. After incorporation, by cutting the length of the roll, the mass may be stripped off in one continuous, coherent sheet, which on exposure to the atmosphere, through which the spirit and camphor are volatilized, hardens to a hornlike mass.

In the manufacture of a smokeless powder by this means, it is customary to mix with the nitro-cotton or mixed cellulose nitrates, a small proportion of other nitrates in order to effect complete combustion and a restrainer to assist in bringing the rate of combustion within normal limits; and this mixing is easily effected on the incorporating rolls. Barium nitrate is the salt which is perhaps most largely used, and it is preferred because it is very permanent, contains a fair proportion of available oxygen which it yields with comparative readiness, and possibly because the carbonate which is formed by the combustion has so high a specific gravity that it settles with considerable speed.

Other solvents besides camphor spirits are employed when the higher cellulose nitrates are used in the manufacture of the powder. Thus Engel takes a cellulose nitrate prepared from wood, while Glaser employs that prepared from paper or cardboard and treats it, when dry, with ethyl acetate or acetone, the action of the solvent being aided by mechanical kneading in a suitable vessel until a viscid paste or gelatinous mass is obtained with which the barium nitrate and a hydrocarbon, such as naphthalene, is incorporated. The mass is then formed into any desired shape and the solvent is allowed to evaporate or is distilled off by any suitable means when the powder is left as a dense horny material, with a glassy fracture, which can be readily granulated.

The first military smokeless powder of the modern class was made in France in 1886 by Vieille, and is said to have been compounded of cellulose nitrates mixed with picric acid, but it was soon abandoned in favor of the Poudre B., which consisted of cellulose nitrates alone, or Poudre B. N., which consisted of these nitrates mixed with barium nitrate and potassium nitrate as oxidants, and sodium carbonate as a neutralizer. Both these mixtures were condensed and hardened to a celluloid-like mass by means of a solvent like ether-alcohol, ethyl acetate or acetone.

Excellent ballistic results have been reported from France as being obtained with these powders, and they have been adopted by the French government. At the same time similar mixed cellulose nitrate powders have been produced and used in Germany, Austro-Hungary and Switzerland; the Weteren, Troisdorf and Von Förster powders being of this class. Notwithstanding that these have so long been known, our government has, with regal graciousness, recently granted a patent to two of its officers for a powder of this composition.

These are made by mixing the ingredients together with the

solvent in a kneading machine of the Werner and Pfleiderer class, in batches of one to two hundred weight, until it is converted into a dough, when it is incorporated and the solvent partly driven off by putting on the grinding rolls, by which means it is also formed into continuous sheets, whose thickness is fixed by the set of the rolls. It is preferable where thick masses are desired to first roll into thin sheets so as to evaporate the solvent as completely as possible from the gelatinized mass, and then by piling the thin sheets on one another, weld them together by running them through the rolls. They are then granulated by passing them under a set of revolving circular knives which cut them first into strips and then into rectangles of the desired size and shape. These powders are dense, hard and hornlike in appearance.

Following Vieille by about two years,[1] Nobel invented ballistite, which practically is a modified explosive gelatine, differing from it only in that while the gelatine consists of ninety-three per cent. of nitroglycerin, and seven per cent. of nitro-cotton, ballastite contains about forty per cent. of nitro-cotton and one to two per cent. of anilin or diphenylamin, which is added to the nitroglycerol nitro-cotton mixture as a neutralizing agent to ensure stability. At first the solution of the gun-cotton and gelatinization of the mixture was effected by means of camphor and later by means of benzene, but it is now produced under the English patent of Lundholm and Sayer of 1889. They discovered that while dry nitro-cotton is but slightly soluble in nitroglycerin even at moderately high temperatures, when mixed with warm water and stirred up by compressed air, gelatinization sets in and solution may be completed by pressing out the water and working in the grinder. Flexible, transparent rubber-like sheets are formed, which may be cut into flakes in cutting machines of the usual type, or in pastry cutters, or may be squirted through spaghetti machines, as is done in Italy, where these cords or threads of ballistite are known as "Filite."

It is curious to note how many of the machines devised for bread making, pastry cutting and macaroni forming, have been employed in the manufacture of smokeless powder.

In 1889 Sir Frederick Abel and Professor James Dewar secured their patents on cordite, which like ballistite, contains nitroglycerin and cellulose nitrate, but whereas ballistite is made from nitro-cotton alone, cordite is made from "gun-cotton" containing from ten to twelve per cent. of nitro-cotton, to which is added a little tannin, dextrin or vaseline to serve as a restrainer. The gelatinization is effected by means of acetone,

[1] English Patent, January 31, 1888.

the mixture being kneaded to a dough in a water-jacketed kneading machine,compacted in a mould in a preliminary press, and the mould transferred to a spaghetti machine, where the explosive is squirted into cords. As these cords issue, they are reeled on bobbins, which are placed in the drying house to drive off the acetone. When this is completed the product of ten pressings is wound from ten one-strand reels on to one ten-strand reel and then the cordite on six ten-strand reels is wound on one drum, making a cord of sixty strands, which in short lengths forms the thirty and one-half grains charge for the magazine rifle. For the higher calibers the cords are cut in lengths as they issue from the press, dried and made up into bundles. Cordite is an elastic rubber-like mass with a light to dark brown color.

Analogous to these in composition, in that they consist of nitroglycerin with cellulose nitrates, are many powders, such as amberite, Maxim's powder, Leonard's powder, P. P. G., Peyton's powder, German smokeless powder and others, and they differ in but slight particulars. Thus Curtis and André *blend different cellulose nitrates* before incorporation so as to secure a definite nitrogen content, and then cement by ether-alcohol; Maxim restrains his powder with castor oil; Leonard restrains his with lycopodium, and adds urea crystals as a neutralizer; Walke claims to make P. P. G. from a nitro-cellulose, which is not gun-cotton, and so on.

The employment of nitro substitution compounds as bases for smokeless powders has been comparatively limited. Over twenty years ago Designolle invented powders made by mixing potassium picrate, potassium nitrate and charcoal in various proportions. Borlinetto produced them from picric acid, sodium nitrate and potassium dichromate. Abel and Brugère from ammonium picrate, potassium nitrate and charcoal, and more recently Nobel from ammonium picrate, barium nitrate and charcoal. Within a few years past a powder has been manufactured in this country and put upon the market as a sporting powder, which was composed of ammonium picrate, potassium picrate, and ammonium dichromate, but I understand it has given such irregular and abnormal pressures that its manufacture has been discontinued.

While these powders may have been smoke-weak as compared with gunpowder, it is difficult to understand how, in the presence of such amounts of metallic radicles, they could have been smokeless. A powder, however, which is made by Hermann Güttler, by dissolving nitro-lignin in molten dinitro-toluene and which he calls Plastomentite, may well possess this property,

and it is reported to have given good ballistic results at the Bucharest tests of 1893.

The powder called Gelbite, and invented by Dr. Stephen H. Emmens, was also smokeless. This was made by an ingenious process in which paper in strips was nitrated to a moderate degree of nitration, then fumed with ammonia to neutralize the acid, and then treated with picric acid to neutralize the ammonia and form ammonium picrate. These strips were then rolled up into rolls as charges, but as might have been foreseen from a study of the behavior of gunpowder in guns and the study of the history of gun-cotton, this powder was too brusque in action and has been abandoned.

I began my own experiments with smokeless powder manufacture in 1889. At this time the remarkable results published from France, and the announcement that that country had adopted a smokeless powder, had produced their desired strategic effect. All her rivals were seeking to be equally well equipped and were hastening to adopt a powder even before its qualities were thoroughly proven. The newspapers contained remarkable accounts of their performances and alleged descriptions of their methods of production, which while interesting as news and conveying valuable suggestions, could not be relied upon as to accuracy in details.

At the outset, being familiar with the impossibility of securing absolute uniformity and constancy of composition in physical mixtures like gunpowder, and realizing how important this feature was with our precise modern weapons, and when employing an explosive possessing great energy, I determined to attempt to produce a powder which should consist of a single substance in a state of chemical purity. This was a thing which I had not known of having been done, nor have I yet learned that any one else has attempted it. Among the bodies at command, the nitric ethers seemed most available, and of these cellulose nitrate seemed for many reasons the most promising.

There are, as you are aware, several of these nitrates (authorities differ as to the number) which differ in their action towards solvents, though all except the most highly nitrated are soluble in methyl alcohol. In the commercial production of cellulose nitrate certainly, and so far as I have observed under all circumstances, when nitrating cellulose the product is a mixture of different cellulose nitrates. Even in the perfected Abel process for making military gun-cotton, as carried out at the Royal Gun Powder Factory, at Waltham Abbey, according to Guttmann[1], the product contains as a rule, from ten to twelve per cent. of nitro-cotton.

[1] Manufacture of Explosives, **2**, 259, 1895.

Consequently I began by purifying my dried pulped military gun-cotton, which was done by extracting it with hot methyl alcohol in a continuous extractor, and when this was completed the insoluble cellulose nitrate was again exposed in the drying room. The highly nitrated cellulose was then mixed with a quantity of mono-nitro-benzene, which scarcely affected its appearance and did not alter its powdered form. The powder was then incorporated upon a grinder by which it was colloidized and converted into a dark translucent mass resembling India rubber. The sheet was now stripped off and cut up into flat grains or strips, or it was pressed through a spaghetti machine and formed into cords, either solid or perforated, of the desired dimensions, which were cut into grains. Then the granulated explosive was immersed in water, boiling under the atmospheric pressure, by which the nitro-benzene was carried off and the cellulose nitrate was indurated so that the mass became light yellow to gray, and as dense and hard as ivory, and it was by this physical change in state, which could be varied within limits by the press that I modified the material from a brisant rupturing explosive to a slow burning propellent.

This is the powder which I styled indurite, and which has been popularly known as the Naval Smokeless Powder.

I was satisfied that I was justified in starting on this new practice in powder-making when I found, on examination of the samples of foreign military powders[1] which later began to reach me officially, that they were heterogeneous mixtures as the old gunpowder is and that they contained matter which was volatile at ordinary temperatures, and when I learned that the nitroglycerin powders cracked from freezing.

I was still more satisfied when I learned the results of the proving tests which were all made except the chemical stability and breaking down tests by naval officers detailed for this purpose at the Proving Ground and elsewhere, and who had no prejudice in its favor. All of the numerous publications which have appeared about it have issued from headquarters, and I present the matter myself here for the first time.

I have appended the data from these trials to this address where, on inspection it will be seen, that after development, the powder in use, in successive rounds, gave remarkably regular pressures and uniform velocities. I was informed by the Chief of the Bureau before the firing trials, recorded in the tables began, that if I could produce a powder giving 2,000 feet initial velocity and but fifteen tons pressure, it would be a complete success. Inspection of the tables show that this was more than realized and that in two successive rounds in the

[1] Table I.

six-inch rapid fire gun, using twenty-six pounds of my powder and a 100 pound projectile, the pressures were 13.96 and 13.93 tons, and the velocities 2,469 and 2,456 feet per second respectively, while according to the Report of the Secretary of the Navy, 1892, page 26, "the powder manufactured for use in the six-inch rapid fire guns was stored at Indian Head proving ground, through a period of six months, covering a hot summer, and at the end of the time showed no change in a firing test."

On page 25 Secretary Tracy says, "It became apparent to the department early in this administration that unless it was content to fall behind the standard of military and naval progress abroad in respect to powder, it must take some steps to develop and to provide for the manufacture in this country of the new smokeless powder, from which extraordinary results had been obtained in Europe. With this object negotiations were at first attempted looking to the acquisition of the secret of its composition and manufacture. Finding itself unable to accomplish this, the Department turned its attention to the development of a similar product from independent investigation. The history of these investigations and of the successful work performed in this direction at the torpedo station has been recited in previous reports. It is a gratifying fact to be able to show that what we could not obtain through the assistance of others, we succeeded in accomplishing ourselves, and that the results are considerably in advance of those hitherto attained in foreign countries."

From this survey we see that all of the smokeless powders that have met with acceptance and proved of value as ballistic agents with the exception of Indurite are mixtures of one or more of the cellulose nitrates, or mixtures of these bodies, with nitroglycerin or some other oxidizing agent, like barium nitrate, and a restrainer or with a nitro substitution compound and that all have been condensed or hardened into a rubber-like or celluloid-like form, by which, even under the high pressures which obtain in the gun, they are expected to undergo combustion only and that at a moderate and regular rate.

In thus condensing the material, and in determining the best form of grain, it will be observed that we have been guided by the experience gained in the compression of gunpowder, and we have been able to effect this as we have by the experience gained in the development of celluloid, and we have been able to manipulate our product and shape it into grains only by adopting the methods and machines developed in the manufacture of food, while we have been able to test our product and check our results and thus ensure a more rapid and

certain advance by the constant use of the pressure gauge and velocimeter. In my opinion, if these resources had not been at command and available the smokeless powder industry would not yet exist.

From what has been said it may properly be inferred that we seek in these new powders all the virtues of the old gunpowder with the addition that the new powder shall be smokeless, impart higher velocities while producing no greater pressures and that less of it shall be required to do the work. These requirements may be summed up as follows :

The conditions that a smokeless powder suitable for a propellent should fulfill are :

1. That it shall be physically and chemically uniform in composition.
2. That it shall be stable and permanent under the varying conditions of temperature and humidity incident to service storage and use for all time.
3. That it shall be sufficiently rigid to resist deformation in transportation and handling.
4. That it shall produce a higher or as high a velocity with as low a pressure as the service charge of black powder for a given piece.
5. That it shall be incapable of undergoing a detonating explosion.
6. That the products of its combustion shall be nearly if not quite gaseous so that there shall be no residue from it and little or no smoke.
7. That it shall produce no noxious or irrespirable gases or vapors.
8. That it shall not unduly erode the piece by developing an excessive temperature.
9. That it shall be as safe as gunpowder in handling and loading.
10. That it shall be no more than ordinarily dangerous to manufacture.

Most of these requirements have been satisfied in several of the powders, but time alone can determine the question of absolute stability and especially as the comparison is instituted with gunpowder which has been under observation for over 500 years.

We can and do apply tests whose results give us some confidence as I did when I exposed Indurite wrapped in felt in an iron vessel to a temperature of 208° F. for six hours without its undergoing change, and again at a temperature of 212° F. for twenty hours before any change was observed, and again to 5° F. without its being affected.

In fact from the outset I have advised the application of most rigid tests and drew up the following scheme for the Navy Department in July, 1891, by which to test Indurite.

"The most important requisite of powder, after passing the proof test, is that it shall retain its characteristics under all the conditions of storage or transportation which may obtain in the service or that, if any change does take place, it shall not cause the powder to develop under the "proof" conditions any greater pressure than it did at the time of proving, and that such falling off in velocity as may result from this change in the powder shall not be relatively greater than that which obtains for service black powder, and shall be uniform for the same conditions of exposure.

"In providing for this test I would first prove a ten pound lot to determine the maximum weight that will come within the limits fixed for pressure and velocity, and then I would load 1000 Winchester 30.1 cal. and 1000 Mannlicher shell with a charge some grains (say five) less than the maximum, so as to be doubly safe in case the pressure should become increased through the treatment to which the powder is subjected.

"The loading should be done with extreme care by skilled workmen in an especially clean and uniformly heated and dried room. The charges should be weighed on chemical balances and with all the precautions surrounding an analytical operation. The balls should be weighed and gauged, and the shell should be gauged so as to secure as nearly absolute uniformity as possible, while the caps and priming (if used) and wads should be identical for each shell of each 1000 lot.

"These being prepared, I would pack these ball cartridges precisely as if ready for issue to the service, and then I would store 385 Winchester's and 385 Mannlicher's in the regular magazine at the Naval Torpedo Station, and the same number of the same kind in the regular magazine at the Naval Ordnance Proving Ground. I would then draw from the magazine at the Torpedo Station twenty-five Winchester's and 25 Mannlicher's and fire them, using the muskets and measuring instruments which are to be used throughout the trials, and I would repeat this trial every month for three years, firing ten rounds of each form of ammunition and using the same muskets and instruments throughout. At the same time I would have an identical set of tests made at the Proving Ground, the same precautions being taken there regarding the instruments and tools. Throughout the tests a close watch should be kept on the magazines by means of maximum and minimum thermometers so that if abnormal results are obtained in firing it may be known whether or

not any abnormal conditions have obtained in the magazine. This series of tests will consume 1540 rounds. It would, in my judgment, be of much value to store with these cartridges and fire with them an equal number of charges of standard service black powder, to be used as a standard for reference by which any error in the observations, or defects in the instruments may be detected.

"I would take eighty rounds of the Winchester's and eighty of the Mannlicher's and place them in an oven heated to 140° F. or thereabouts. At the end of one month twenty of each are to be drawn out and this to be repeated each month for four months. One half of each form should be proved at the Torpedo Station and the other half at the Proving Ground.

"I would take eighty rounds of the Winchester's and eighty of the Mannlicher's and subject them for two weeks to the freezing temperature, then for two weeks to a temperature of about 140° F., and then draw twenty of each, and this should be continued until the last forty drawn out have been exposed for eight weeks to freezing and eight weeks to the high temperature. The firing trials with these should be made as with preceding ones.

"The remaining shell should be stored in the regular magazine to be used in any test case which may arise or in any manner suggested by the results obtained in the tests described above.

"In the meantime tests could be made with the hand cut S. P. for the capacity of the powder to resist crumbling and dusting during transportation and the tendency of the fixed ammunition to explode *en masse* by the impact of projectiles, or by the explosion of a single cartridge in the midst of a box filled with them. The first can be effected by taking a pound or a kilogram of carefully sifted powder, placing in a copper vessel which it only partly fills, and attaching it to a shaft so that it will be continually and violently shaken, and allowing this to go on every working day for a week. The powder can then be sifted, using the same mesh as before, the weight of the dust found and the percentage of dusting for the given circumstances determined.

"In the trials for tendency to explode *en masse* fifty or forty-five caliber ammunition can be used and the weights of charges need not be very precise, but the ammunition should be packed in, as nearly as possible, the same way as would obtain in service practice."

We have seen that the development of smokeless powder has been rendered necessary by the improvement in the gun. It now appears that in consequence of the possession of the powder

we must further improve the gun for we cannot in our present guns utilize all the energy now available. Experiments looking to this have been going on in France, where in a Canet ten cm. gun of eighty calibers, with a charge of 12.35 pounds of powder and a projectile weighing 28.66 pounds there was obtained the extraordinary muzzle velocity of 3366 feet per second, while the maximum pressure was 18.91 tons per square inch. Longridge, an English authority, deprecates the lengthening of the gun as it becomes too unwieldy and he advocates utilizing the energy of the gun by strengthening it so it will endure greater pressures and then using larger charges. He points out that if this Canet gun were reduced to forty-five calibers, and strengthened, we could obtain from it the same enormous muzzle velocity by increasing the charge to thirteen and a half pounds, though the pressure would rise to twenty-five tons per square inch.

What the result will be where authorities of standing disagree is impossible to foresee, but the fact is demonstrated that the powder is now more highly developed than the gun, and that while seeking for smokelessness, we have secured a propellent which is capable of producing much higher velocities than gunpowder, with all the additional advantages of flat trajectory, increased danger area, greater accuracy, and greater range which follow as consequences.

TABLE I.

COMPOSITION OF VARIOUS POWDERS.

Mark.	Nitro-Cotton.	Guncotton.	Barium Nitrate.	Potassium Nitrate.	Sodium Carbonate.	Volatile.	Cellulose.	Sodium Picrate.	Charcoal.	Humus.	Nitro-Glycerin.	Graphite.
B. N., Aug. 22, '90	26.84	44.42	18.25	3.08	4.92	2.05	....	....	....	....	....	....
B. N., Dec. 5, '90	29.79	40.54	19.00	5.81	3.87	1.50	....	....	....	....	....	....
B. N., June 3, '91	38.05	35.55	18.94	1.81	4.51	1.06	....	....	....	....	....	....
B. N., Aug. 12, '91	41.31	29.13	19.00	7.97	2.03	1.43	....	....	....	....	....	....
B. N., Oct. 16, '91	31.38	49.89	17.92	3.43	2.82	0.82	....	....	....	....	....	....
B. N_A., July 9, '90	31.27	40.52	18.42	6.62	2.58	1.25	....	....	....	....	....	....
B. N_C., Aug. 22, '90	32.62	39.44	18.90	7.45	1.39	1.63	....	....	....	....	....	....
B. N_C., Dec. 5, '90	32.03	39.52	19.36	5.17	3.75	0.92	....	....	....	....	....	....
B. N_I., Oct. 16, '91	72.09	26.49	....	....	....	0.92	0.47	trace	....	....	....	....
French Powder, June 3, '91	73.11	25.98	....	....	....	0.89	....	trace	....	....	....	....
Poudre B., Oct. 16, '91	32.86	66.00	....	....	....	1.14	trace	....	....	....	....	....
Walsrode, S. P., Sept. 4, '90	12.08	86.28	....	....	0.93	0.72	....	....	....	....	....	....
[1]Wetterin, S. P., March 18, '91	46.70	30.35	....	....	....	9.66	....	....	12.39	0.90	....	....
[2]Wetterin, S. P., March 18, '91	48.15	30.73	....	....	....	8.22	....	....	12.12	0.77	....	....
[3]Wetterin, S. P., March 18, '91	47.78	25.87	....	....	....	14.69	....	....	10.84	0.80	....	....
Lebel, Sept. 27, '90	28.21	69.45	....	....	0.80	1.49	....	....	....	....	....	....
German, Oct. 15, '90	10.00	88.43	....	....	0.56	0.99	trace	....	....	....	....	....
Cordite, Sept. 17, '90	7.04	29.20	....	....	[4]6.17	1.30	0.23	....	....	....	56.04	....
Cordite, Oct. 11, '90	8.45	27.72	....	....	[4]4.23	1.45		....	....	....	58.13	....
Ballistite, Sept. 19, '90	44.58	....	....	....	2.44	....	....	....	....	....	52.99	....
Nobel's, S. P., Oct. 15, '90	53.26	0.97	....	....	3.42	0.41	....	....	....	....	41.95	....
Schwab, Nov. 7, '90	77.41	20.42	....	....	0.69	1.47	....	....	...	...	....	trace

[1] Small arm. [2] Small cube. [3] Large cube. [4] Includes dextrine.

Mark.	Nitro-Cotton.	Guncotton.	Barium Nitrate.	Potassium Nitrate.	Sodium Carbonate.	Volatile.	Cellulose.	Sodium Picrate.	Charcoal.	Humus.	Nitro-Glycerin.	Graphite.
[1] Reg. Y., 283, Nov. 14, 90	56.46	....	....	....	0.37	0.33	....	....	....	....	42.84	trace
[2] Reg. Y., 283, Nov. 14, '90	52.10	....	....	...	0.36	0.39	....	....	....	....	47.17	....
German, S. P., Aug. 7, '91	48.83	7.45	....	....	....	0.53	....	....	....	....	43.15	trace
Maxim, flat, June 3, '92	8.14	71.19	....	....	2.58	0.19	....	....	....	....	[3]17.90	....
Maxim, cord, June 3, '92	6.84	46.60	....	....	1.70	0.26	....	....	....	....	[3]44.60	....
									Manchester yellow			
Rifleite, May 7, '92	22.48	74.16	....	....	....	0.84	....	....	2.52	....	....	trace
									Aurine			
S. K., May 6, '92	20.39	57.73	18.08	1.24	....	1.43	....	....	1.11	....	....	....
S. R., May 7, '92	28.18	46.97	19.97	2.35	....	1.45	....	....	1.06	....	....	....
	[4]lignin	[5]lignin			$NaNO_3$		[6]lignin		Aurine			
E. C., Nov. 9, '91	53.57	1.86	34.26	1.48	3.07	1.17	3.12	....	0.55	....	....	....
									Paraffin			
Schultze, Sept. 24, '91	27.71	32.66	27.62	2.47	2.88	1.48	1.63	....	4.20	....	....	....
Brackett, Sept. 26, '91	31.43	13.70	....	....	19.76	2.93	13.22	....	....	18.94	....	....
American Wood Pd., Jan. 27, '91	24.90	30.07	....	....	9.76	5.83	19.55	....	....	9.89	....	....
" Grade C., Aug. 27, '91	29.25	14.06	....	....	15.27	3.01	28.08	....	....	10.32	....	....
" " E., Aug. 27, '91	24.91	25.62	....	....	17.81	3.86	19.15	....	....	8.65	....	....
" 10-Bore Trap, Aug. 29, '91	33.21	18.69	....	....	14.82	2.36	20.27	....	....	10.65	....	....
" 12-Bore Trap, Aug. 31, '91	29.47	21.85	....	....	13.38	3.14	16.59	....	....	15.62	....	....
					sodium picrate							
Reine Powder, Dec. 8, '90	....	....	48.44	....	46.31	1.18	....	....	Charcoal 4.07	....	....	....

[1] Five mm. [2] One mm. [3] Includes castor oil. [4] Soluble nitro-lignin. [5] Insoluble nitro-lignin. [6] Unconverted lignin.

TABLE II.

TESTS OF INDURITE AT NAVAL ORDNANCE PROVING GROUND.

Powder.	*Gun.*	*Weight of Charge.*		*Projectile. System.*	*Weight.*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
Service Black.	Hotchkiss 1 Pdr.	140 grams	Small ignition disk in each charge.	Housing	465 grams	11.2	1694
"	"	150 "		"	450 "	11.2	1690
"	"	150 "		Common shell	450 "	....	1793
"	"	150 "		"	450 "	....	1841
S. P. No. 151, No. 3 T.	"	50 "		"	450 "	....	1341
"	"	70 "		"	450 "	....	1811
"	"	80 "		"	450 "	....	2150
"	"	80 "		Housing	460 "	13.0	1877
"	"	80 "		"	460 "	15.0	1896
"	"	75 "		Common shell	450 "	....	1816
"	"	75 "		"	450 "	....	1760
"	"	75 "		"	450 "	....	1894
S. P. No. 153, No. 4 T.	"	70 "		Housing	465 "	14.2	1774
"	"	70 "		"	465 "	14.4	1616
"	"	70 "		Common shell	450 "	About 12.13 tons	1774
"	"	70 "		"	450 "	"	1776
S. P. No. 157, No. $4\frac{3}{16}$ T.	"	70 "		Housing	465 "	8.2	1082
"	"	90 "		"	465 "	11.2	1363
M. N. 2.	"	100 "	Ignition charge 8 grams. N. X. 9 (Blk. fine grain). Ignited at rear.	"	....	13.5	Lost—missed wires
"	"	90 "		Common shell	Not obs.	Not obs.	1584
"	"	90 "		"	....	9.0	1281
S. P. No. 140.	Hotchkiss 3 Pdr.	100 "		"	3 pounds	1.5	882
"	"	200 "		"	3 "	4.3	Lost
"	"	300 "		"	3 "	15.0	2186
"	"	300 "		"	3 "	12.2	Lost
"	"	300 "		"	3 "	12.0	Lost
"	"	300 "		"	3 "	12.3	2105
"	"	310 "		"	3 "	14.9	2216
"	"	310 "		"	3 "	14.8	2250
S. P. No. 148.	"	275 "		"	....	....	....
"	"	300 "		"	....	9.0	1766

Tests of Indurite at Naval Ordnance Proving Ground.

Powder.	*Gun.*	*Weight of Charge.*			*Projectile. System.*	*Weight.*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
S. P. No. 148.	Hotchkiss 3 Pdr.	315	"	Small ignition disc. Priming R. N. X. Q. 89.	Common shell	....	10.4	1921
"	"	325	"		"	....	11.2	2017
"	"	335	"		"	....	12.2	2076
"	"	338	"		"	....	11.0	1995
"	"	345	"		"	....	15.4	2187
"	"	340	"		"	....	14.3	2166
"	"	340	"		"	....	11.5	2126
"	"	343	"		"	....	18.0	2214
S. P. No. 153, No. 4 T.	"	250	"		"	3.3 lbs.	11.3	1887
"	"	275	"		"	3.3 "	13.6	2051
"	"	300	"		"	3.3 "	24.0	2281
"	"	275	"		"	3.3 "	16.8	1975
"	"	270	"		"	3.3 "	14.5	2000
"	"	270	"		"	3.3 "	16.0	2018
"	"	270	"		"	3.3 "	22.5	2050
S. P. No. 141 a.	Hotchkiss 6 Pdr.	200	"	Ignition charge 8 grams N. X. L., Blk. fine grain.	"	6 "	7.2	1085
"	"	250	"		"	6 "	9.0	1237
"	"	300	"		"	6 "	9.2	1453
"	"	300	"		"	6 "	9.2	1453
"	"	325	"		"	6 "	9.6	1584
"	"	350	"		"	6 "	9.6	1648
"	"	375	"		"	6 "	13.6	1813
"	"	375	"		"	6 "	10.6	1738
"	"	400	"		"	6 "	16.0	1903
"	"	390	"		"	6 "	14.3	1841
"	"	392	"		"	6 "	14.3	1855
S. P. No. 153, No. 4 T.	"	200	"		"	6 "	6.5	1330
"	"	250	"		"	6 "	8.6	1544
"	"	300	"		"	6 "	9.9	1679
"	"	350	"		"	6 "	16.7	1728
"	"	340	"		"	6 "	15.0	Lost

Tests of Indurite at Naval Ordnance Proving Ground.

Powder.	Gun.	Weight of Charge.			Projectile. System.	Projectile. Weight.		Pressure. Tons.	Velocity. Foot—seconds.
S. P. No. 153, No. 4 T.	Hotchkiss 6 Pdr.	340	"	Priming 8 grams N. X. L.	Common shell	6	lbs.	18.0	Lost
S. P. No. 157, No. 4⅞ T.	"	300	"		"	6	"	5.0	1324
"	"	350	"		"	6	"	6.5	1473
"	"	400	"		"	6	"	11.4	1775
"	"	420	"		"	6	"	9.1	1738
S. P. No. 148, No. 4.	"	300	"		"	6	"	7.6	1543
"	"	350	"		"	6	"	11.1	1751
"	"	365	"		"	6	"	12.0	1818
"	"	372	"		"	6	"	12.5	1835
"	"	382	"		"	6	"	11.0	1862
"	"	392	"		"	6	"	13.0	1920
"	"	410	"		"	6	"	13.6	2002
"	"	418	"		"	6	"	15.0	2047
"	"	418	"		"	6	"	15.0	2047
S. P. No. 148, No. 4.	"	418	"		"	6	"	14.8	2043
"	"	418	"		"	6	"	14.0	2012
"	"	418	"		"	6	"	13.0	1992
M. N. 2.	"	400	"		"	6	"	9.5	1724
"	"	480	"		"	6	"	11.6	1988
"	"	480	"		"	6	"	12.0	1992
"	"	440	"		"	6	"	8.0	1702
"	"	450	"		"	6	"	8.0	1728
"	"	450	"		"	6	"	8.1	1735
S. P. No. 146 b.	4-in. No. 11.	4.5	pounds	Priming charge 25 grams of fine grained powder in each charge.	"	33	"	13.5	1762
S. P. No. 146 a T.	"	4.5	"		"	33	"	10.9	1820
S. P. No. 149 T.	"	2.25	"		"	33	"	3.5	1177
"	"	4.50	"		"	33	"	10.3	1845
"	"	4.75	"		"	33	"	11.5	1945
"	"	5.00	"		"	33	"	13.6	2046
"	"	5.15	"		"	33	"	14.0	2080
"	"	5.25	"		"	33	"	14.2	2083

Tests of Indurite at Naval Ordnance Proving Ground.

Powder.	*Gun.*	*Weight of Charge.*		*Projectile. System.*	*Weight.*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
S. P. No. 149.	4-in. No. 11.	5.00 lbs.		Common shell	33 lbs.	13.6	Lost
"	"	5.35 "		"	33 "	15.2	Lost
"	"	5.30 "		"	33 "	15.0	1943
"	"	5.30 "		"	33 "	15.0	2122
S. P. No. 159 M.	"	3.5 "		"	33 "	9.5	Lost
"	"	4.05 "		"	33 "	10.3	1912
"	"	4.2 "		"	33 "	11.0	1936
"	"	4.8 "	Ignited at rear.	"	33 "	12.0	1990
"	"	5.2 "		"	33 "	14.7	2125
"	"	5.2 "		"	33 "	14.8	2134
"	"	5.3 "		"	33 "	14.8	2145
S. P. No. 149 M.	"	5.3 "		"	33 "	15.0	2160
"	"	5.3 "		"	33 "	14.8	2158
S. P. M. N. 2 (163).	"	4 "		"	33 "	7.5	1591
"	"	5 "		"	33 "	10.2	1888
"	"	5.5 "		"	33 "	12.35	1993
"	"	5.5 "		"	33 "	12.35	1997
"	"	4 "		"	33 "	7.3	1606
"	"	4 "	One ignition grain in base of each charge. Ignition at rear.	"	33 "	7.2	1569
"	"	5 "		"	33 "	10.5	1892
"	"	5 "		"	33 "	10.2	1865
S. P. No. 159 M. N. 2.	6-in. No. 120.	9.5 "		"	77 "	6.5	1728
"	"	13½ "		"	77 "	10.0	2131
"	"	15 "		"	77 "	11.9	2281
"	"	16½ "		"	77 "	13.6	2415
S. P. M. N. 3, No. 162.	"	11½ "		"	100 "	5.0	1466
"	"	15 "		"	100 "	7.9	1784
"	"	18 "		"	100 "	11.0	2060
"	"	20 "		"	100 "	13.2	2212
"	"	21 "		"	100 "	14.4	2312
" After 6 mos.	"	14 "		"	100 "	6.7	1678
" storage.	"	20 "		"	100 "	12.0	2170

Tests of Indurite at Naval Ordnance Proving Ground.

Powder.	*Gun.*	*Weight of Charge.*	*Projectile. System.*	*Weight*	*Pressure. Tons.*	*Velocity. Foot—seconds.*
S. P. M. N. 6.	6-in. No. 120.	15 "	Common shell	100 lbs.	5·06	1535
"	"	19 "	"	100 "	7·30	1793
"	"	23 "	"	100 "	11·20	2151
"	"	25 "	"	100 "	12·56	2369
"	"	26 "	"	100 "	13·96	2469
"	"	26 "	"	100 "	13·93	2456
S. P. M. N. 3, No. 162.	"	7 "	"	50 "	4	1496
"	"	11 "	"	50 "	10	2108
"	5-in. "	7 "	"	50 "	4	1496
"	"	11 "	"	50 "	10	2108
"	"	12 "	"	50 "	12	2256
"	"	12·75 "	"	50 "	13·2	2383
"	"	13·12 "	"	50 "	14·2	2474
"	"	13·4 "	"	50 "	15·6	2578
S. P. M. N. 2 (168).	4-in. R. F. No. 8.	5½ "	"	33 "	12·4	1997
"	"	5½ "	"	33 "	13·4	2042

ACIDITY OF MILK INCREASED BY BORACIC ACID.

By E. H. Farrington.

Received July 22, 1896.

WHILE making some investigations with milk preservatives, the writer noticed that sweet milk in which a small quantity of boracic acid (preservaline) was dissolved, required what appeared to be an abnormally large quantity of one-tenth normal alkali to neutralize it and much more than water in which the same amount of "preservaline" was dissolved. One-half gram of preservaline was dissolved in 500 cc. water, and twenty cc. of this solution required one cc. of one-tenth normal alkali to produce the pink color, when phenolphthalein was used as an indicator in titrating. Before adding preservaline the water had a neutral reaction.

One-half gram preservaline was dissolved in 500 cc. of sweet milk, and twenty cc. of it required eight cc. of one-tenth normal alkali to give the pink color, although before adding the preservaline twenty cc. of this same milk gave the pink color with only four cc. of one-tenth normal alkali.

The same amount of preservaline increased the acidity of a given quantity of milk four times as much as it did the acidity of the water.

The writer is unable to explain this reaction, but it gives a simple means of detecting preservaline or boracic acid in milk, as normal milk will smell or taste sour when it contains as much natural acidity as is represented by eight cc. of one-tenth normal alkali to twenty cc. milk. This represents 0.36 per cent. lactic acid, and it can be safely stated that milk which contains over three-tenths per cent. lactic acid and neither tastes or smells sour, has been adulterated with some preservative, probably boracic acid.

Dairy School,
University of Wisconsin.

CORRESPONDENCE.

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., JULY 23, 1896.

Editor Journal of the American Chemical Society, Easton, Pa.:

DEAR SIR:—A majority of the Executive Committee has decided to call the annual meeting of the Association of Official Agricultural Chemists for Nov. 6, 7 and 9, 1896. These dates immediately precede the meetings of the Association of Agricultural Colleges and Experiment Stations, which will convene in Washington, Nov. 10. The session will be held, as heretofore, in the lecture hall of the National Museum, at Washington, D. C.

The Ebbitt House offers to the Association entertainment at the rate of $3.00 per day and the free use of its parlors for committee meetings, if desired. The Ebbitt House is on the corner of "F" and 14th Sts., and can be reached from all stations by the "F" St. or Avenue cars.

Respectfully,

H. W. WILEY,
Secretary A. O. A. C.

BOOKS RECEIVED.

Bulletin No. 42. Second Series. Horticulture. Louisiana State Experiment Station, Baton Rouge, La. 1896. 44 pp.

Bulletin No. 123. Examination of Food Products sold in Connecticut. Connecticut Agricultural Experiment Station, New Haven, Conn. July, 1896. 79 pp.

Transactions of the American Institute of Mining Engineers. Vol. xxv. February to October, 1895, inclusive. New York City: Published by the Institute. 1896. xvii, 1068 pp.

Part III. Geology and Agriculture. A preliminary report upon the Florida parishes of East Louisiana and the Bluff. Prairie and Hill Lands of Southwest Louisiana. By W. W. Clendenin, A.M., M.S., Geologist. Louisiana Experiment Station, Baton Rouge, La. 96 pp.

ERRATA.

On page 667, August number, 12th line from bottom, in equation, for $o.3b$ read $o.3y$.

On page 668, 2nd line from top, for *Dividing* read *Multiplying*.